



BELSŐ ÉGÉSŰ MOTOROK EMISSZIÓTECHNIKÁJA 2.

Belső égésű motorok emissziótechnikája

A katalizátorok

Oktatási segédanyag
tanulói egyéni használatra

összeállította:

Dr. Nagyszokolyai Iván



Kezdjük a szikragyújtásúakkal !

Otto-motor – benzinüzemű, gázüzemű

Szikragyújtású motor

Fremdzündung Verbrennungsmotor

Spark Ignition Engine

Positive Ignition (ICE PI) – UNO ECE

Kezdetben volt az oxidációs katalizátor...

**A három
komponensre ható
(redox)**

katalizátor

Az az emissziótechnika, ami megmentette az Otto-motort anno, az 1970-es évek végén, az a technika mind a mai napig, az Euro 6 előírás követelményénél is a megoldást jelenti és várhatóan a jövőben is.

TWC - Three Way Catalytic Converter (three-way catalysts)

Drei Wege Katalysator

Három-utas katalizátor

Három komponensre ható katalizátor

Redox katalizátor

Vajon miért?

Mi a feladat?

A szénmonoxid (CO),
a szénhidrogének (HC)

és a

nitrogénoxidok (NO, NO₂)

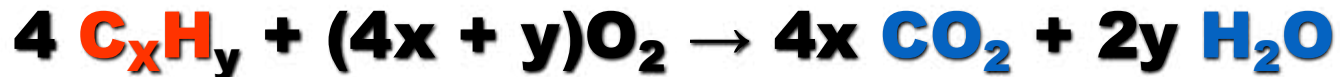
egyidejű, segédanyag nélküli semlegesítése,

tehát

redukálás és oxidálás,

**A katalizátornak kettős feladata van:
oxidálnia és redukálnia kell.**

oxidáció



redukció



Reakcióegyenletek

Oxidation Reactions



NO Reduction Reactions

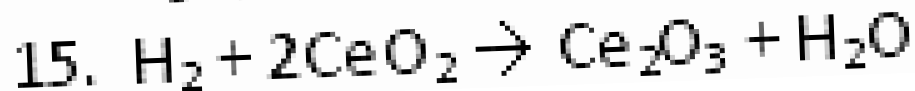
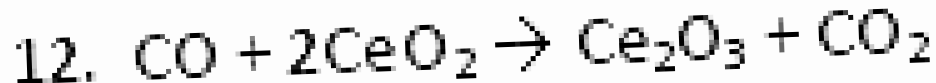
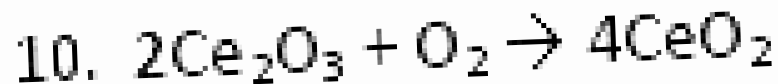


Reakcióegyenletek

Water-Gas and Steam Reforming Reactions



Ceria Reactions (Oxygen Storage)

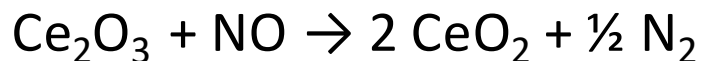


The University of Stuttgart and Volkswagen (2003-01-1001) reported results from a mathematical model of a TWC operating in a high conversion SULEV system based on the following reactions:

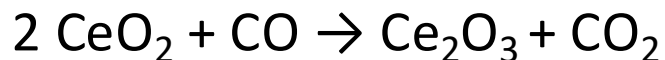


A cérium oxigéntároló tulajdonsága

A cérium oxigéntároló tulajdonsága és hatása abból ered, hogy három- és négyértékű oxidokat képez. Oxidáló körülmények között a következő reakciók játszódhatnak le:

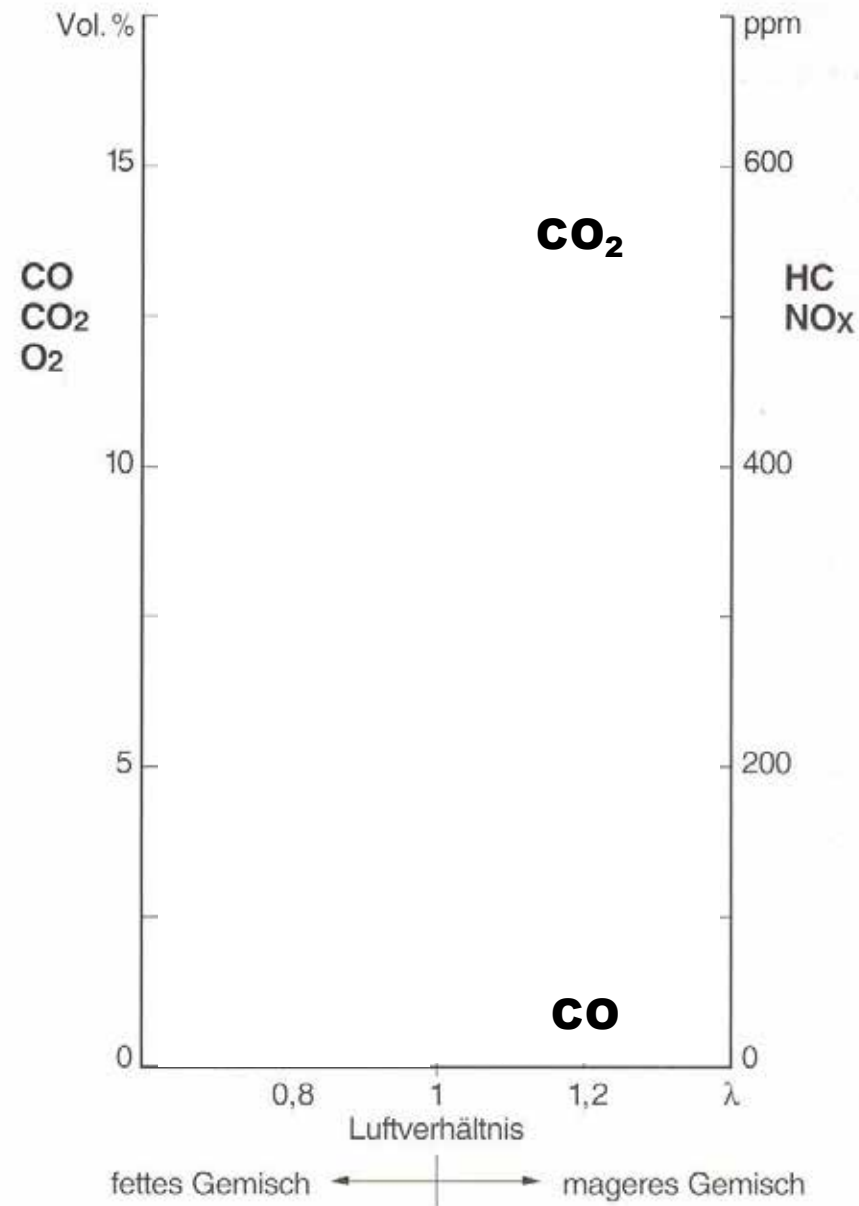


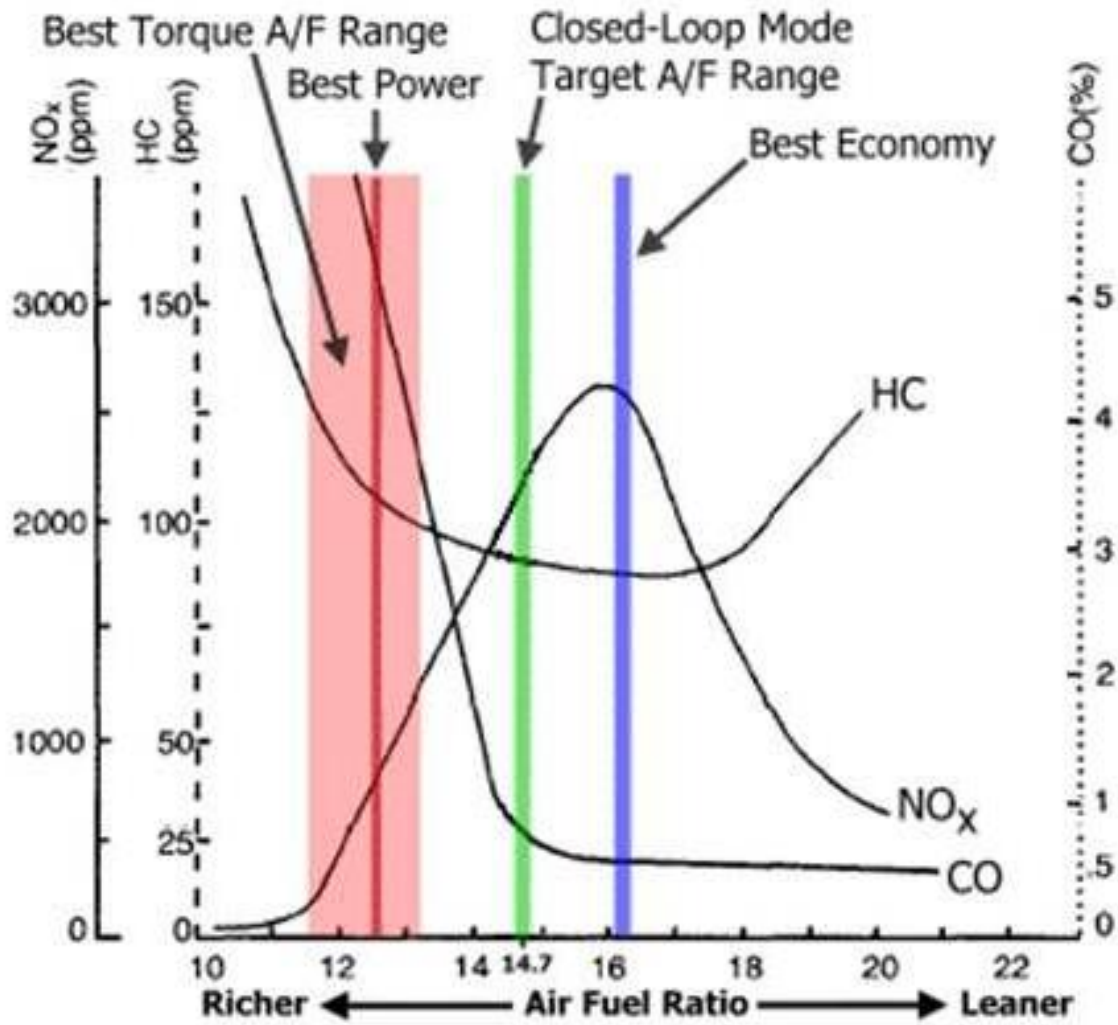
Redukáló körülmények között (dús keverék) viszont a CeO_2 oxidálószerként viselkedhet:



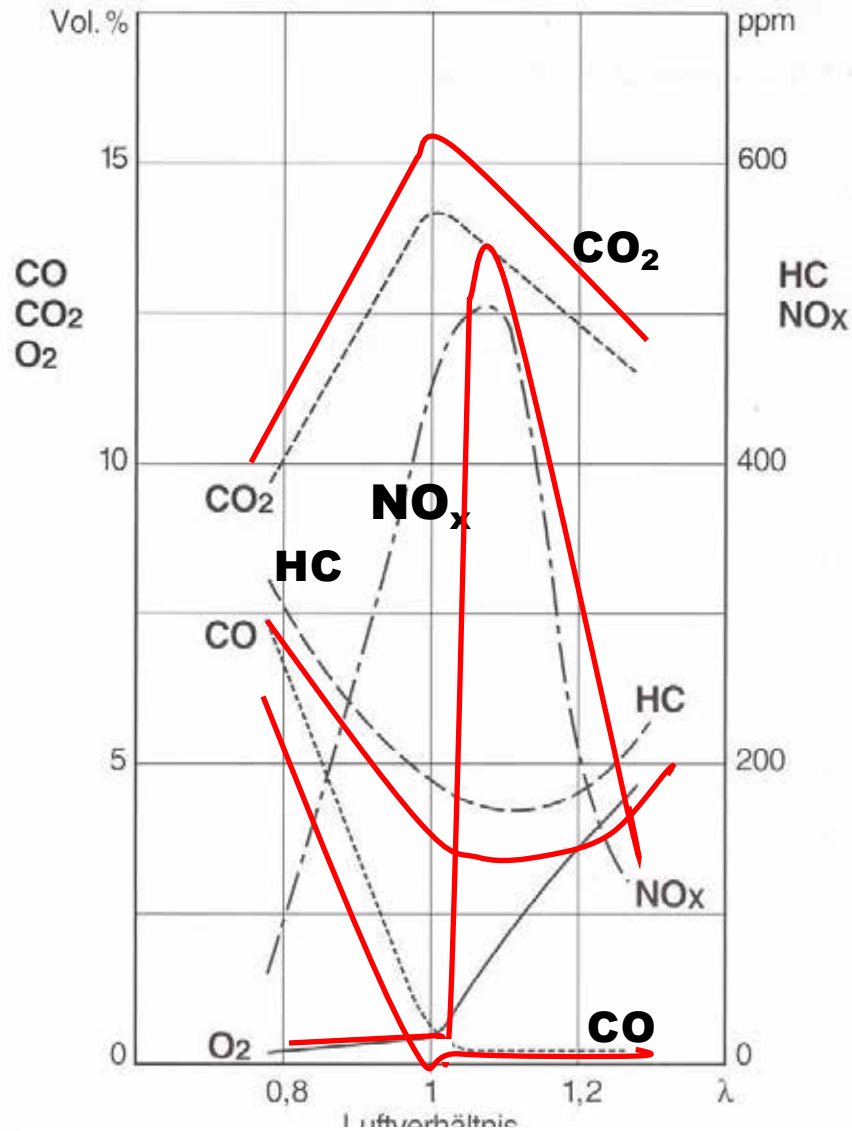
Ce_2O_3 Cérium(III)oxid

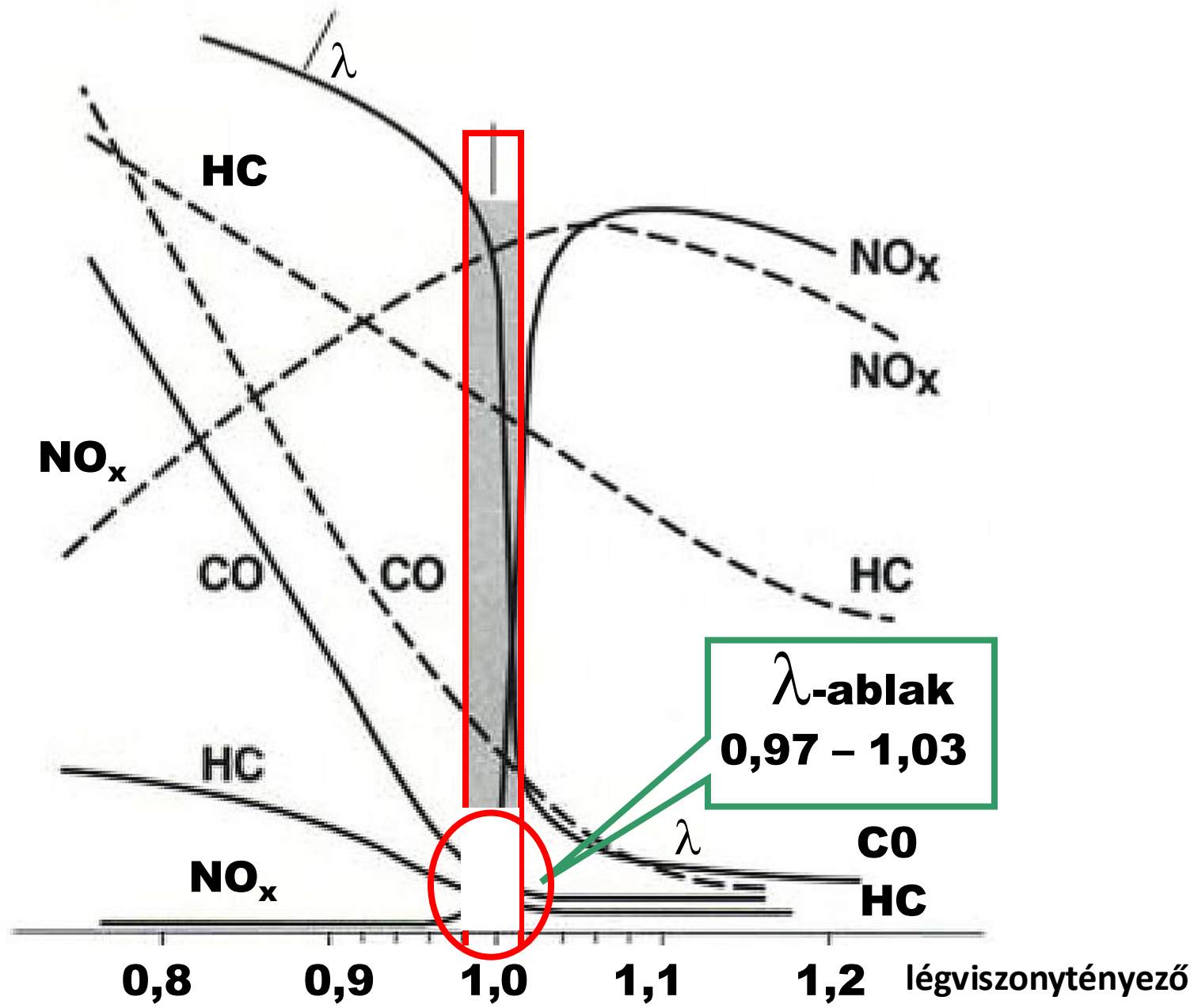
CeO_2 Cérium(IV)oxid





A **redox** katalizátorból kilépő anyagok koncentrációja a légviszony függvényében (nagy motorterhelés)





λ -ablak
0,97 - 1,03

CO
HC

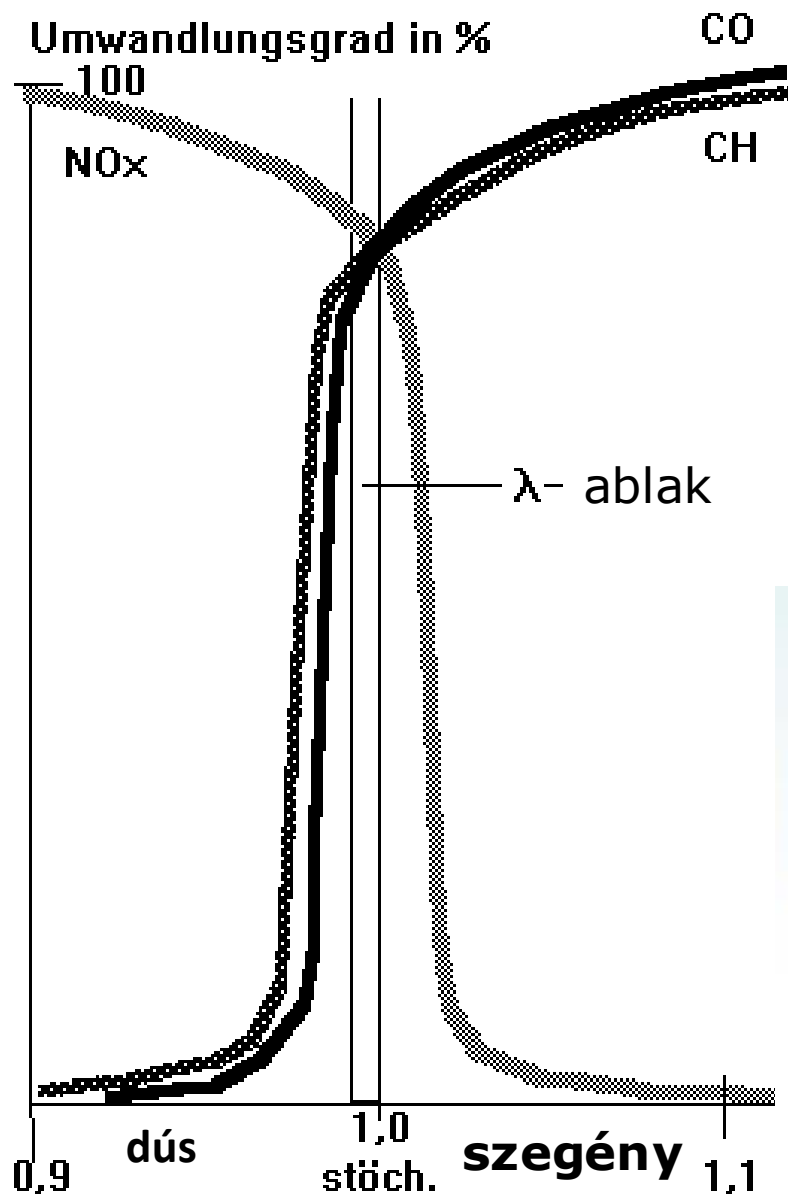
légviszonytényező

One of the first Bosch Lambda Sensor types, late 1970ies, part of Bosch Archives collection

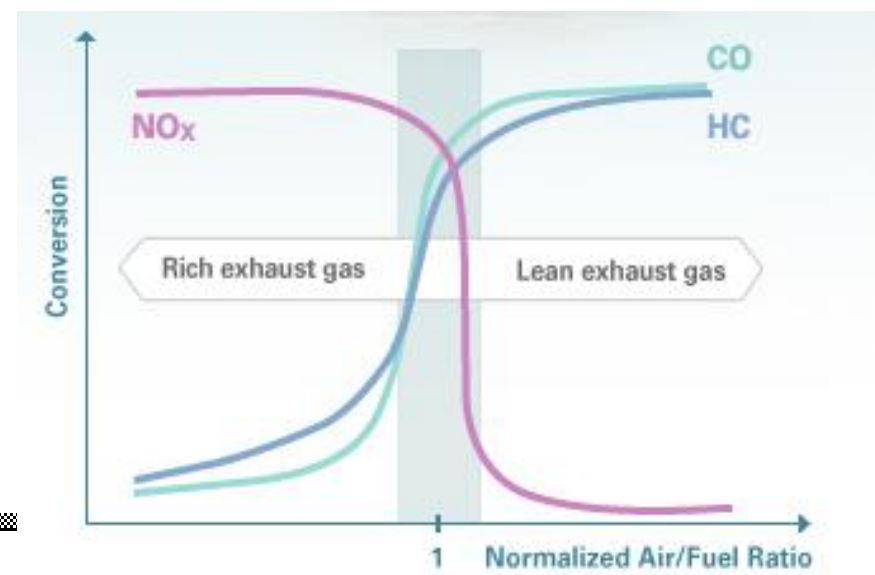


In 1977 U.S. manufacturer Ford sealed a supply deal with Robert Bosch GmbH for more than three million units per year. By 1982 it was heatable, 30 seconds after the engine was started from cold.

A variation on the zirconia sensor, called the "wideband" sensor, was introduced by NTK in 1992.



Átalakítási hatásfok %



Around 1950

The French engineer **Eugene Houdry** invented the automotive catalyst and founded the Oxy-Catalyst Company.

Eugène Jules Houdry ([Domont](#), April 18, 1892 – [Upper Darby, Pennsylvania](#), July 18, 1962) was a French, later naturalised American, [mechanical engineer](#) (graduated from [École Nationale Supérieure des Arts et Métiers](#) in 1911) who invented [catalytic cracking](#) of petroleum feed stocks.

Oxy-Catalyst

After World War II, Houdry formed the Oxy-Catalyst Company and turned his attention to reducing the health risks associated with the increasing amounts of automobile and industrial air pollution. His generic catalytic converter, which greatly reduced the amount of carbon monoxide and unburned hydrocarbons in automobile exhausts, was granted U.S. Patent 2,742,437 in 1956.

A katalizátor feltalálója

- Erfinder: Eugene Houdry
- Houdry machte sich Gedanken über den Einfluss von Autoabgase
- er gründete die Oxy-Catalyst Company → zuständig für Entwicklung von Abgaskatalysatoren von Benzinmotoren
- Houdry = seiner Zeit voraus → 1956 Patent für die Kats
- ABER: Am Antiklopffmittel der Katalysatoren war Blei, welches die Autoabgaskatalysatoren vergiftete.

Oxy-Catalyst

After World War II, Houdry formed the Oxy-Catalyst Company and turned his attention to reducing the health risks associated with the increasing amounts of automobile and industrial air pollution. His generic catalytic converter, which greatly reduced the amount of carbon monoxide and unburned hydrocarbons in automobile exhausts, was granted U.S. Patent 2,742,437 in 1956.



[Chemist Carl D. Keith](#) and John J. Mooney with their team at [Engelhard](#) came up with the first production [catalytic converter](#) in 1973. The three-way catalyst developed by them allowed all three exhaust pollutants (hydrocarbon, carbon monoxide and nitrogen oxides) to be remedied using a single catalyst bed.



John J. Mooney (1929 -)



Carl D. Keith (1920 – 2008)



Harendra Sakarlal Gandhi
(Haren, as he was known)
1941.05.02.–2010.01.23.

US National Medal of Technology
for research, development and
commercialisation of
automotive exhaust catalyst
technology and precious
metal utilisation that he received
from President
George W. Bush in 2002.

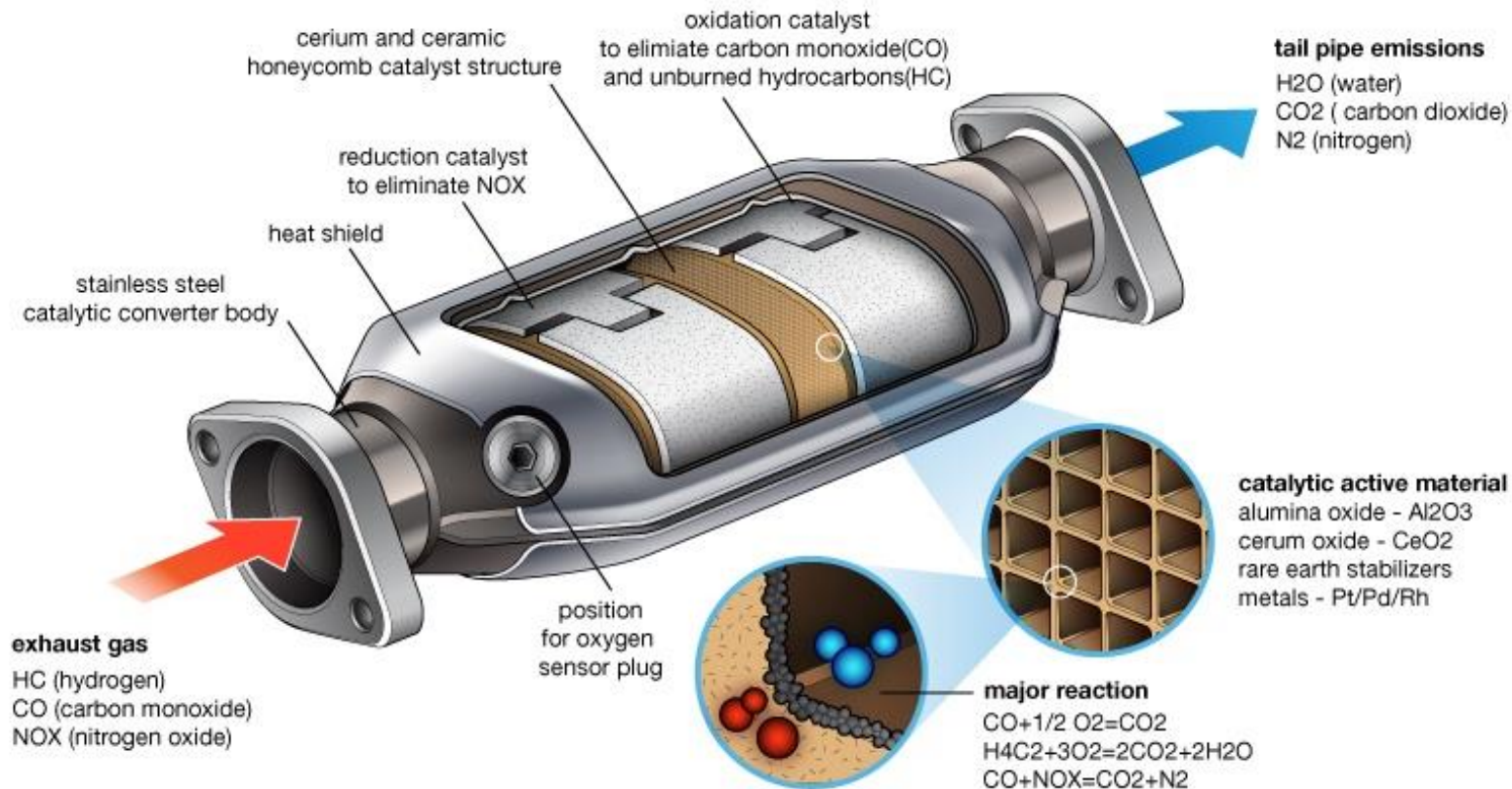
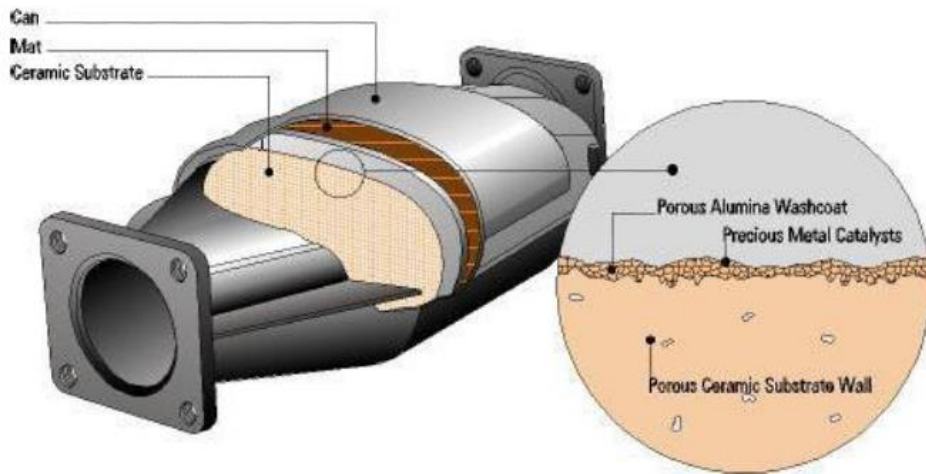
*Throughout his long and distinguished career with the **Ford Motor Company Haren Gandhi** was concerned with controlling tailpipe pollutants from cars, and through his work this article reviews the huge amount of progress made during his **four-decade career**. His early work with gasoline engines embraced all of the major developments ranging from the **first platinumbased oxidation catalysts** through nitrogen oxides (NO_x) reduction using platinum-rhodium catalysts and the later introduction of palladium into **three-way catalysts (TWCs)** via ‘trimetal’, palladium-rhodium and palladium-only formulations. Gandhi’s other work included the interactions of poisons with catalysts as part of maintaining their in-use performance, The potential for using ruthenium in NO_x control in gasoline TWCs and NO_x adsorbing catalysts (NACs) for leanburn engines, and the use of zeolite-based selective catalytic reduction (SCR) catalysts for effective diesel engine NO_x control.*

A TWC katalizátor felépítése

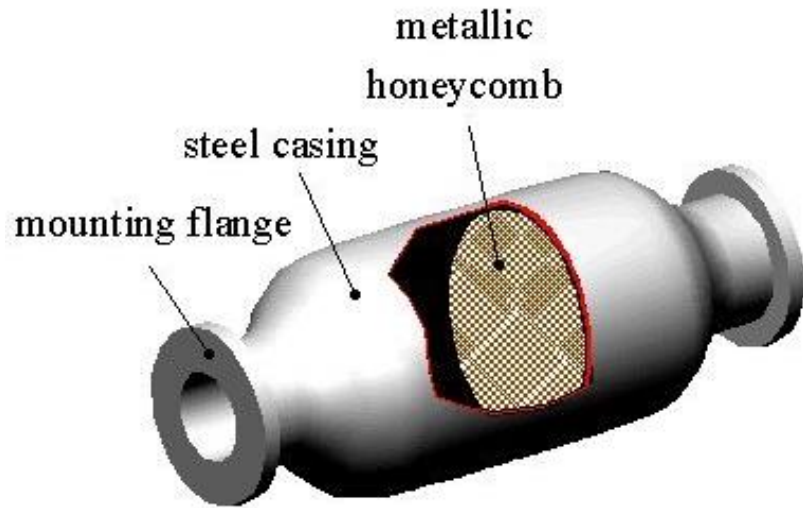




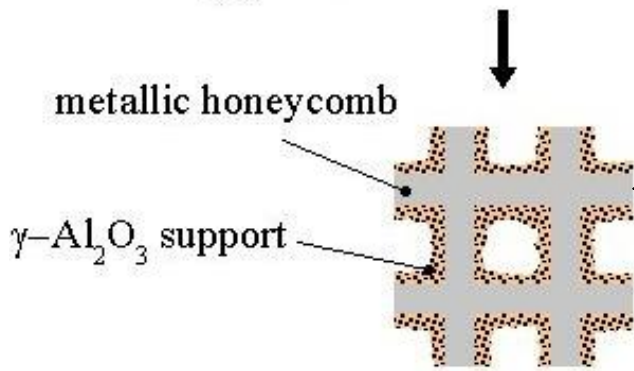
A TWC katalizátor felépítése



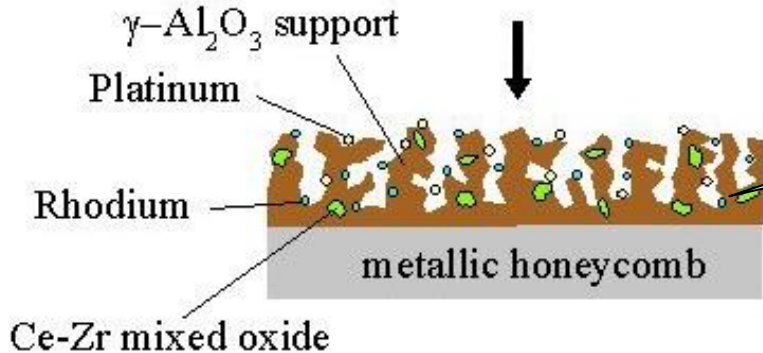
Vázkerámia Rodney Bagley, Irwin Lachman és Ronald Lewis Corning Glass. Bekerültek az USA National Inventors Hall of Fame (2002)



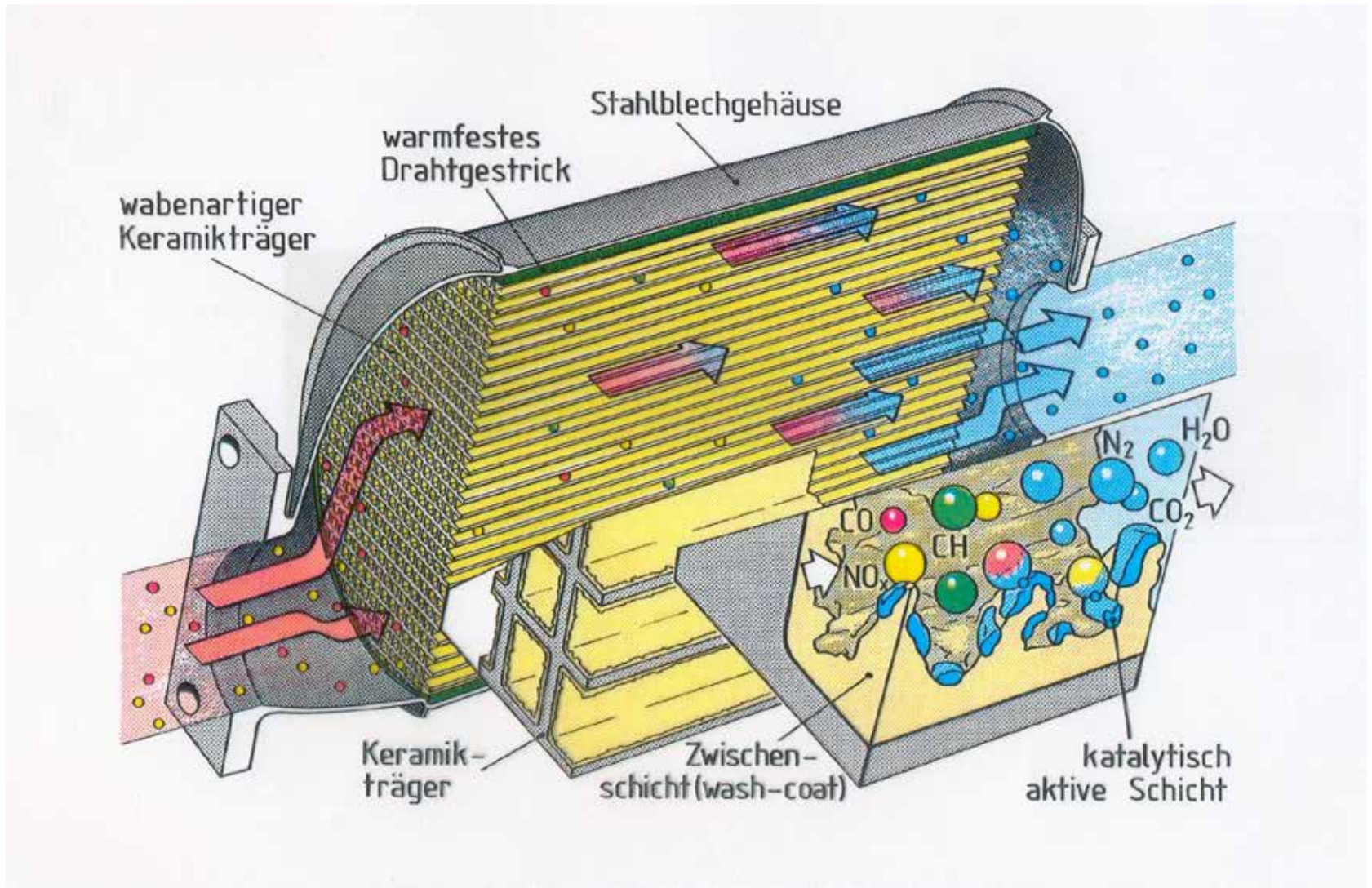
Szubsztrát, support
kordierit vázkerámia
kerámia monolit

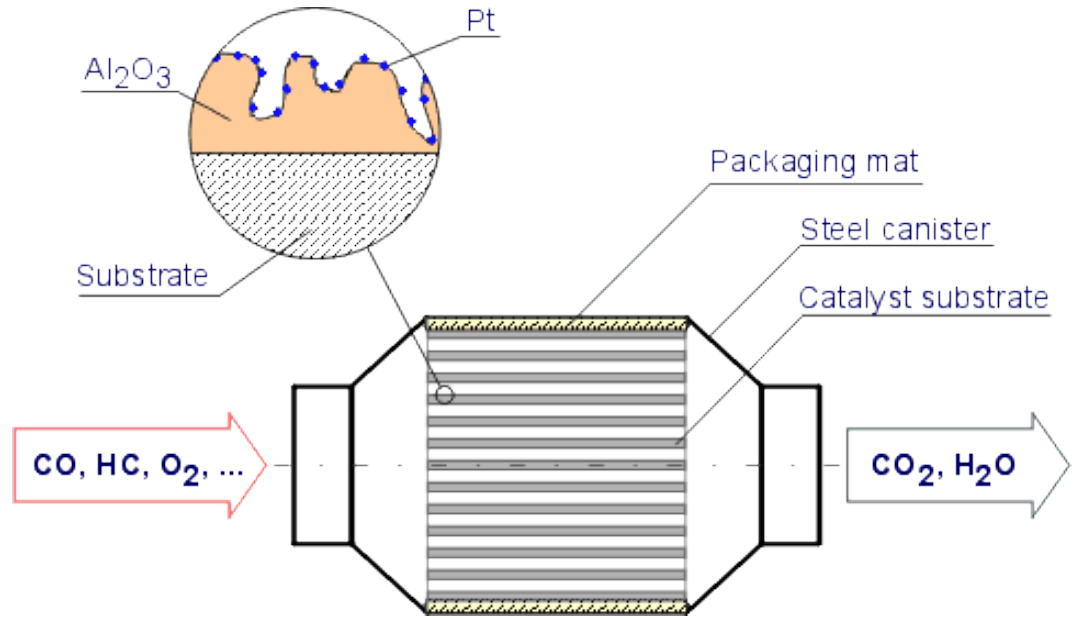


Washcoat
anyaga: fénoxidok



A hármas hatású, redox katalizátor





A hordozó
(szubsztrátum)

substrate

Al_2O_3 kerámiák

(alumíniumtrioxid - alumina)
magnézium-alumínium-szilikátok

Kaolinnal, agyaggal, korunddal és mullittal
adalékolt talkumok.

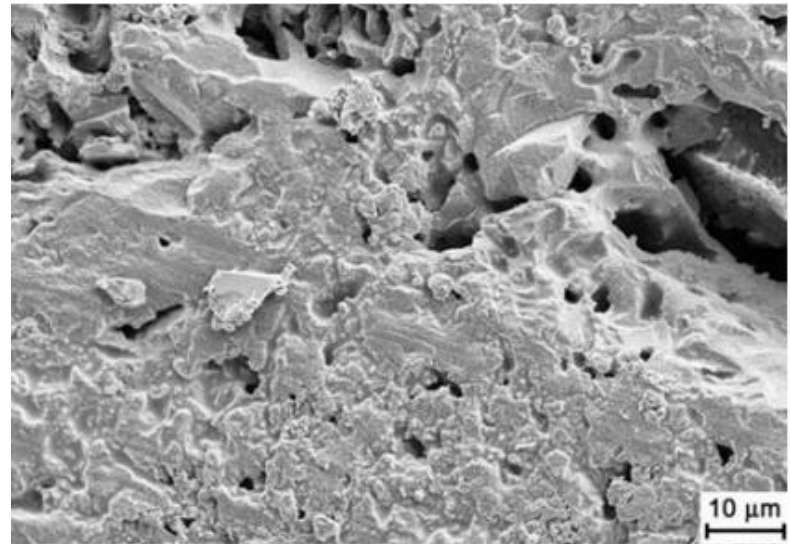
A kordieritek általános kémiai összetétele:

14 % MgO, 35 % Al_2O_3 and 51 % SiO_2

A kordieriteknek kicsi a hőtágulási
együtthatójuk,

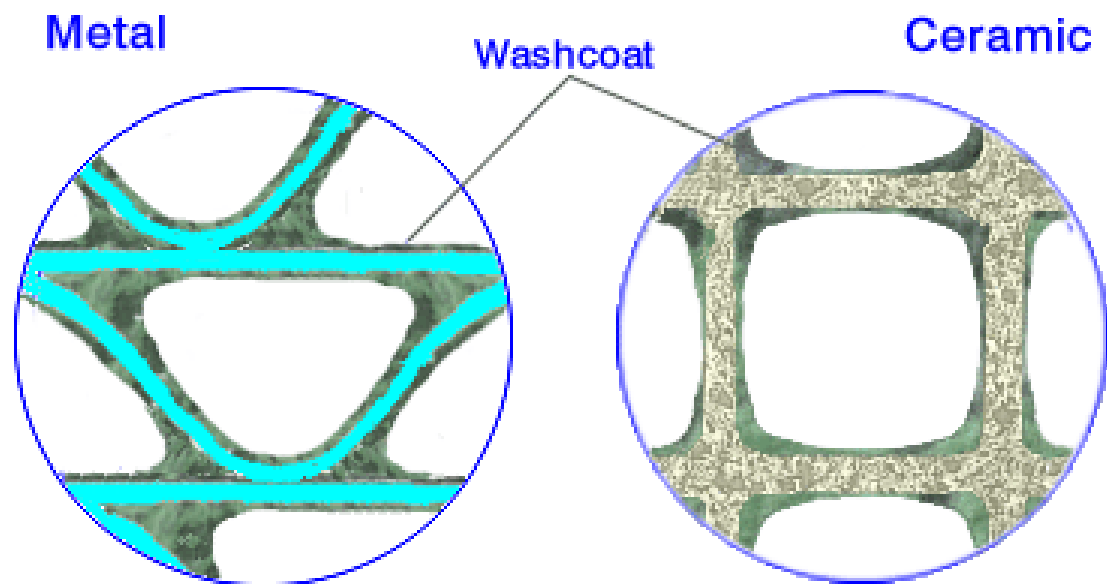
kiváló hőszokk állósági követelmények mellett
nagy szilárdságúak.

Megkülönböztetünk porózus és tömör
kordieriteket.



Specifications Cordierite /kordierit

| | |
|---|--------------|
| Molecular Weight (g/mol.) | 595 |
| Bulk Density (g/cm ³) | 0.42 |
| Thermal conductivity (cal/s-cm-°C) | 0.002 |
| Melting Point (°C) | ~1179- 1471 |
| Specific Gravity (g/cu m) | ~2.3 |
| Specific heat @25°C (cal/g-°C) | 0.35 |
| Color | tan |
| Mohs Hardness | 7 |
| Water Absorption % at room temperature | 0.02 to 3.2 |
| Thermal Expansion (in/in°C (20deg. C-700 deg.C) | 2.3 X10-6 |
| Specific Gravity | 2.6- 2.7 |
| Crystallography | orthorhombic |





Patent megalkotói:

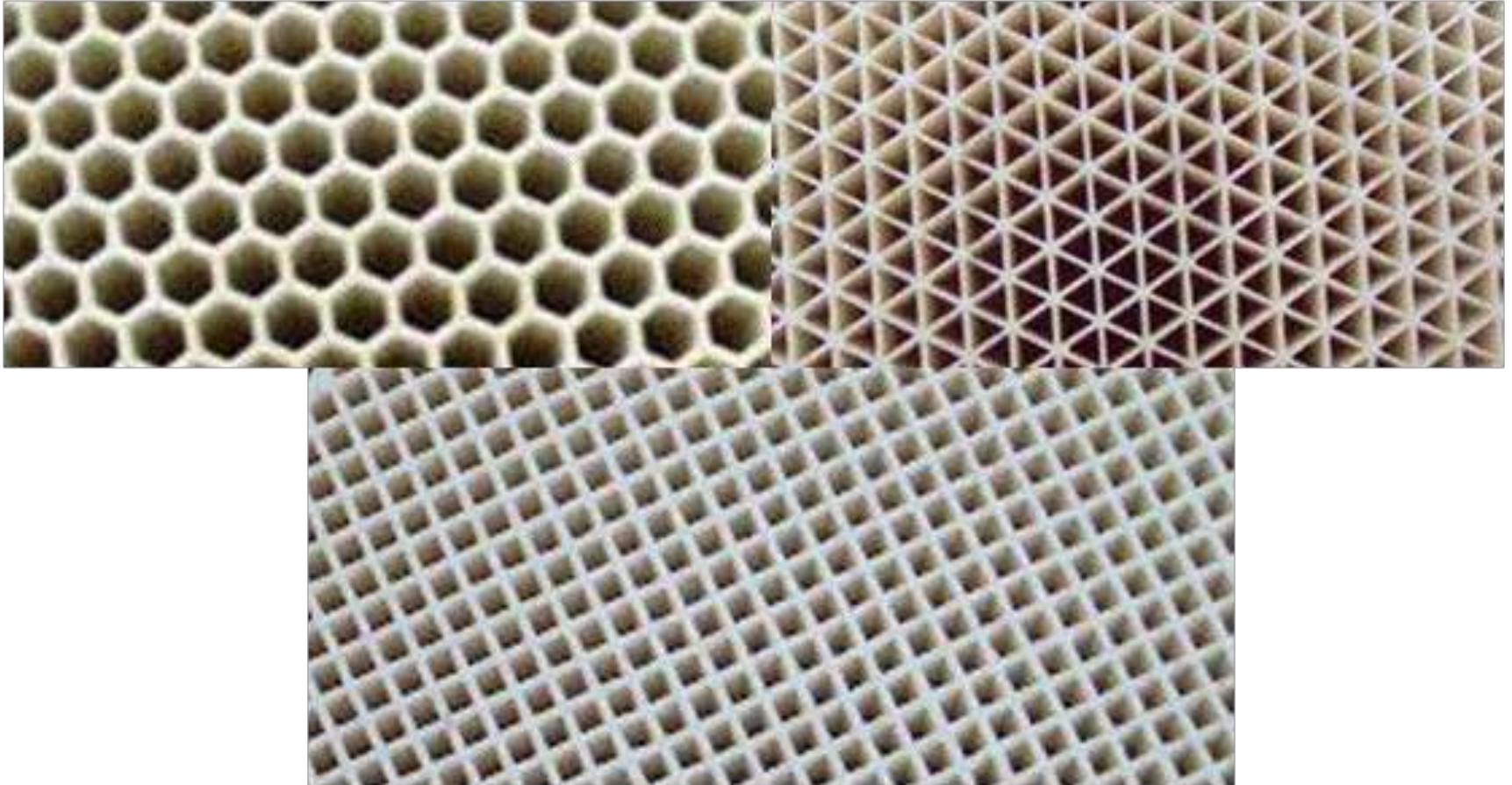
Bagley,
Chman és
Lewis
Glass.

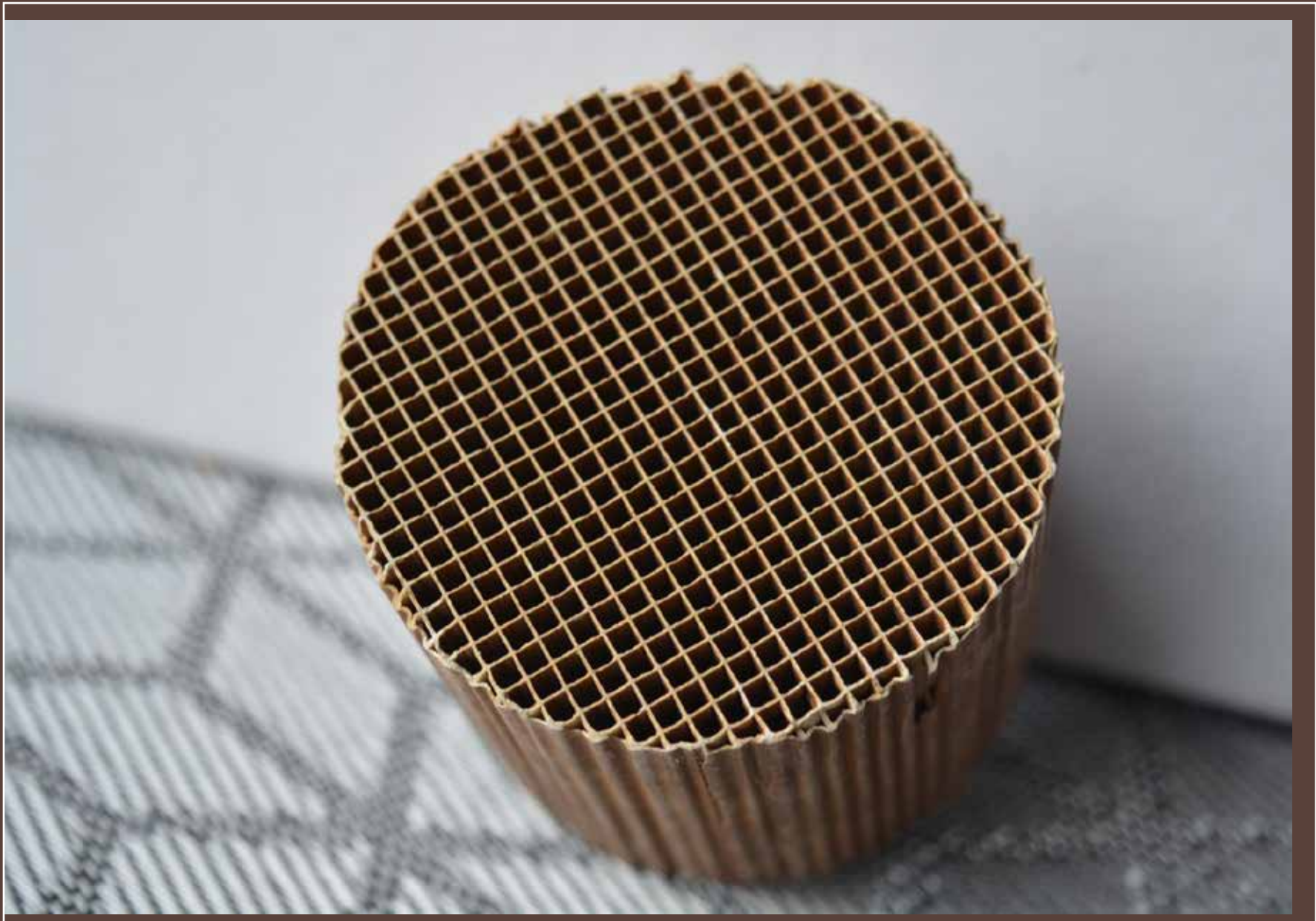
Patent az USA
Inventors
name (2002)

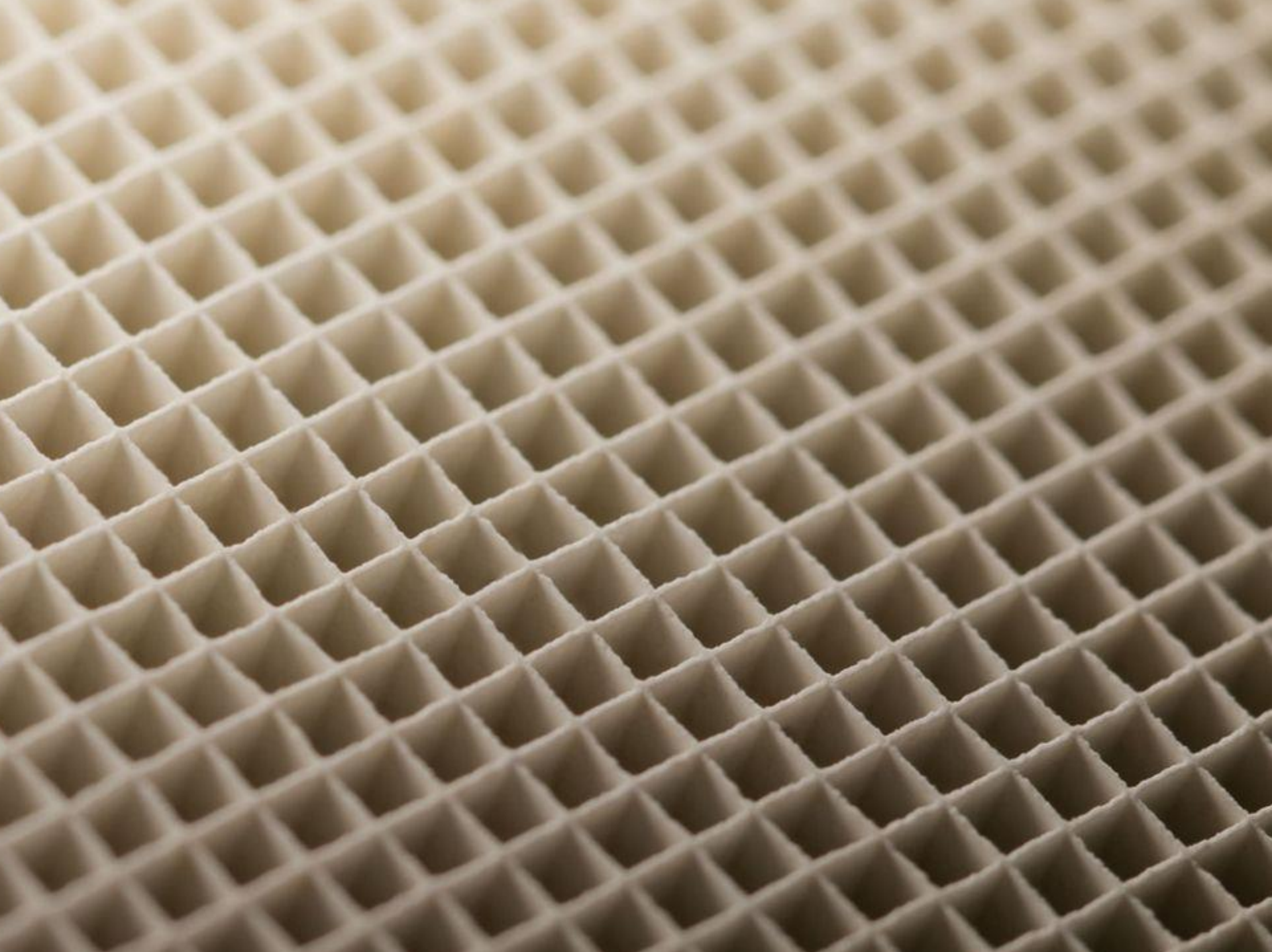
Corning® FLORA™
Substrates

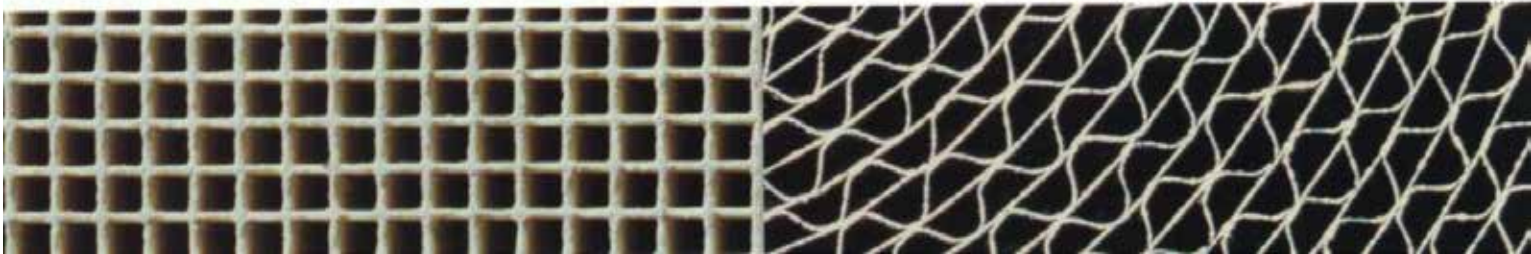
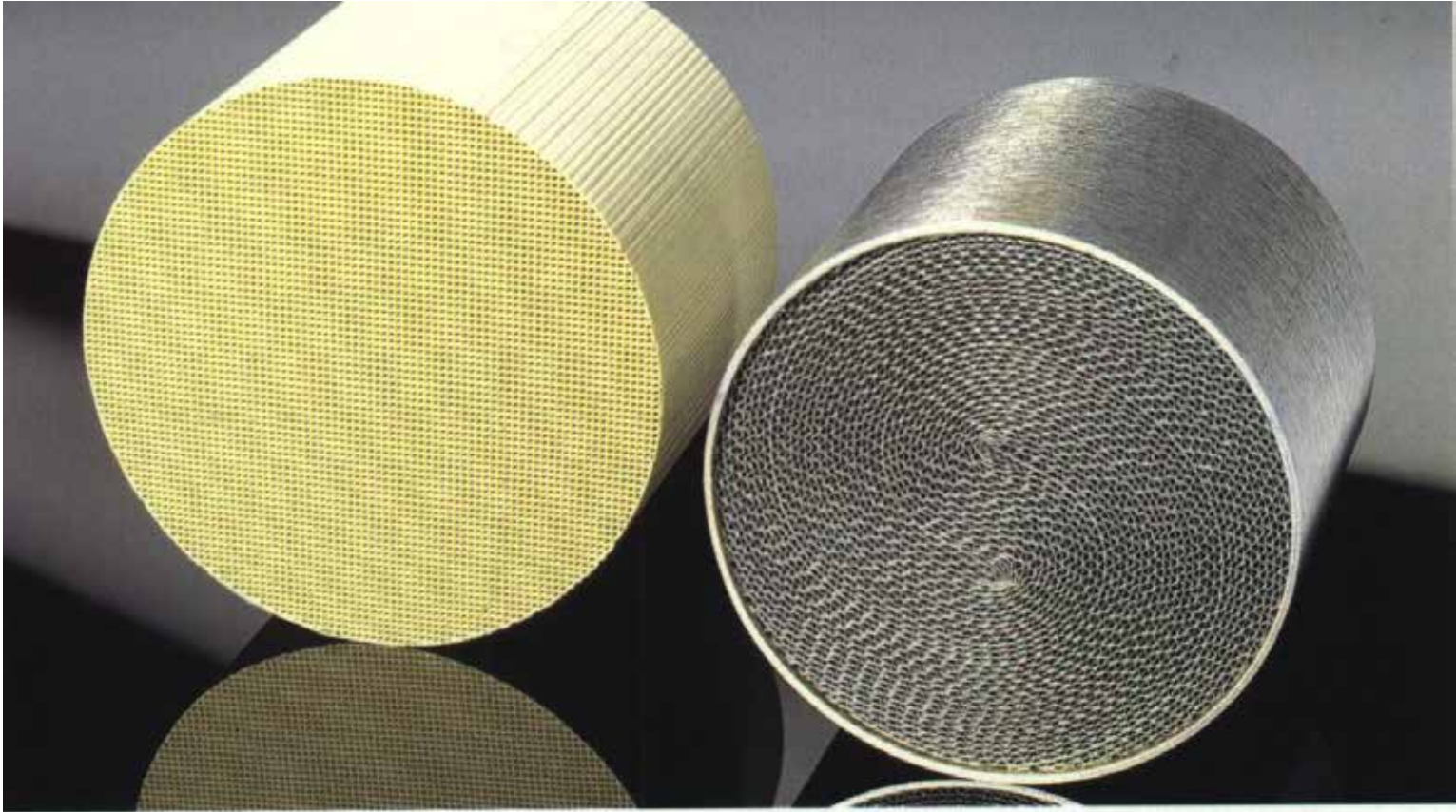


Honeycomb - méhsejt



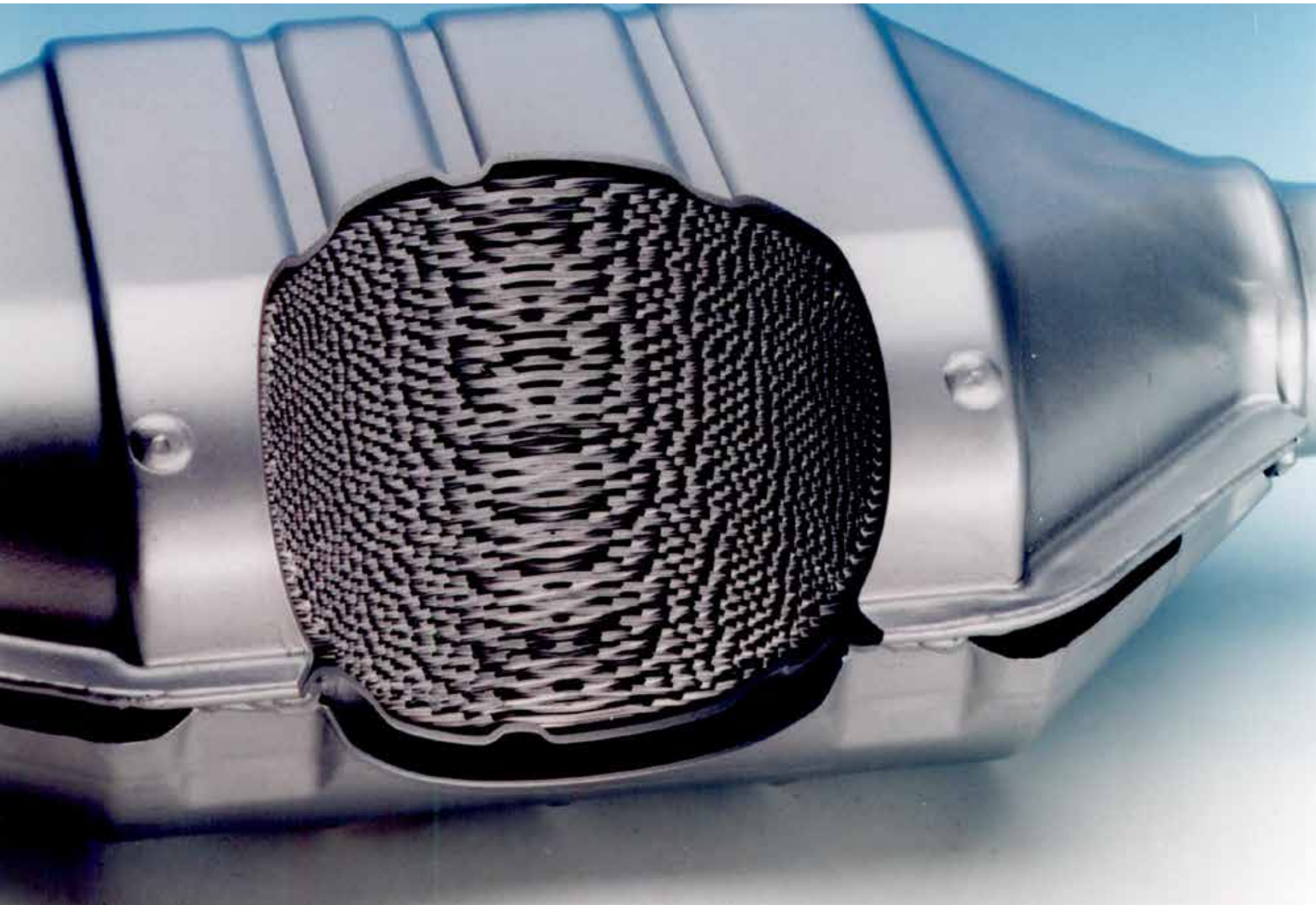


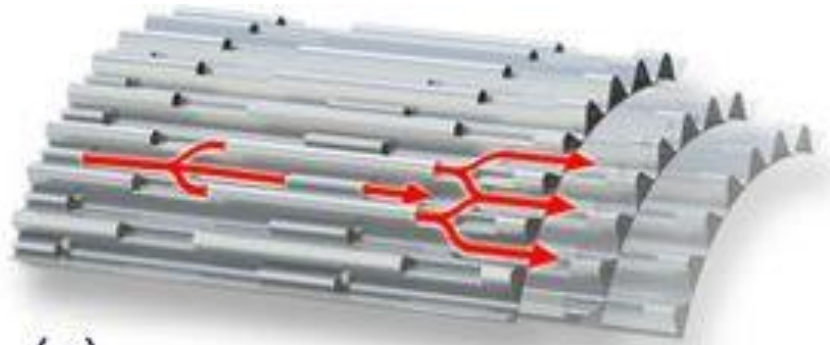




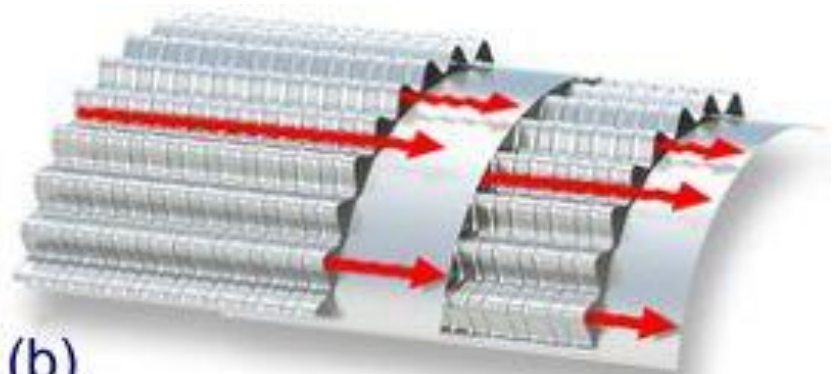




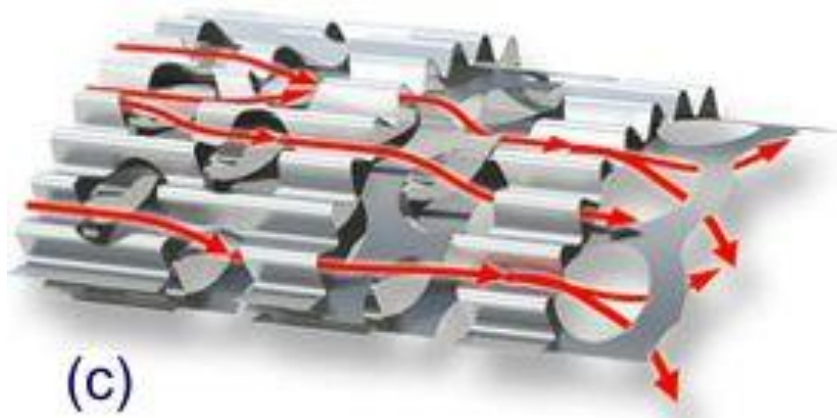




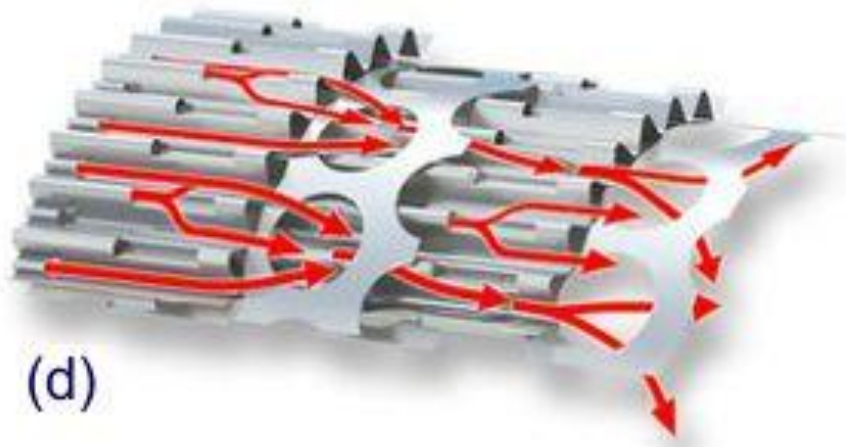
(a)



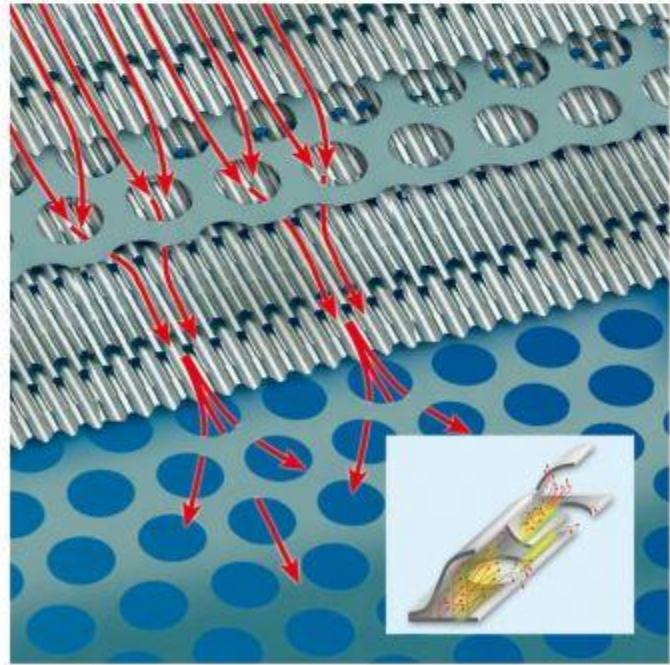
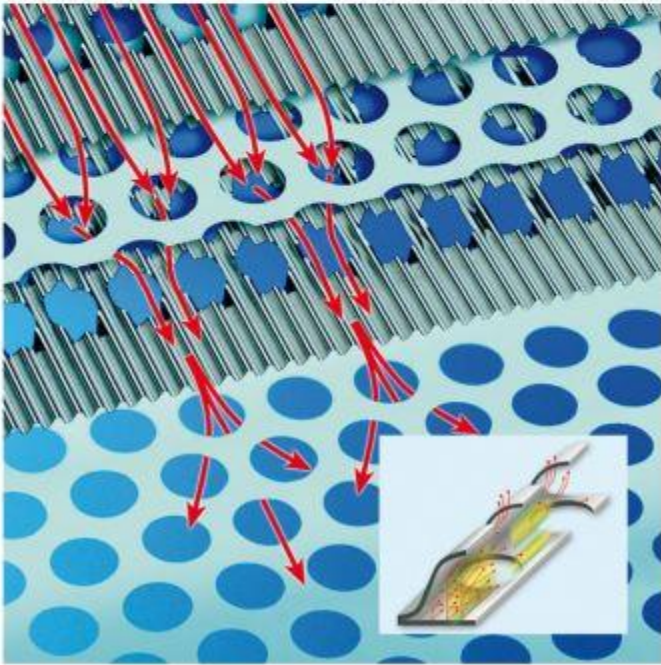
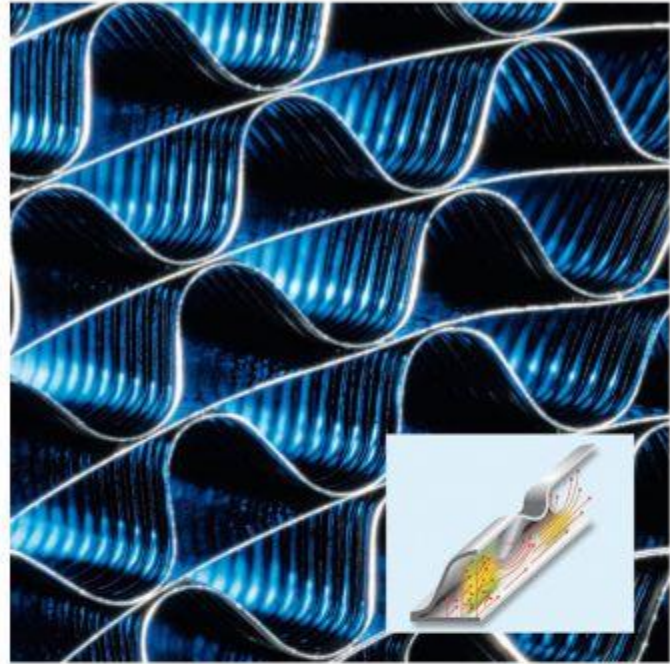
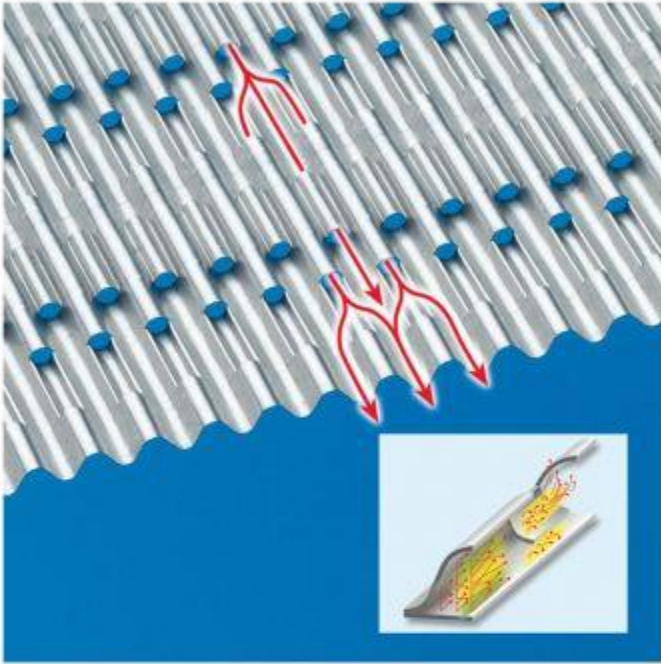
(b)



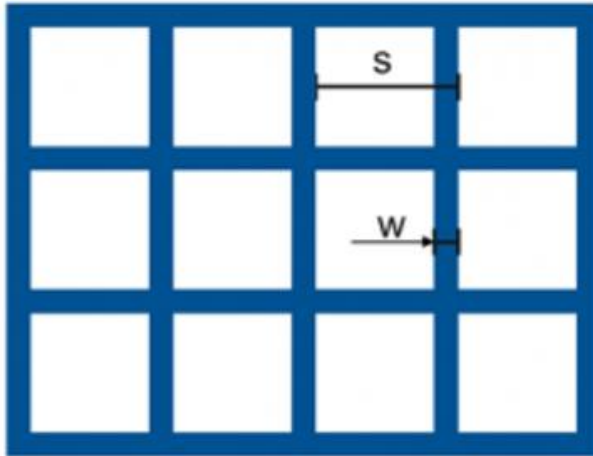
(c)



(d)



A kerámiaváz geometriai méretei, jellemzői



- s = repeat distance
- w = wall thickness
- N = cell density ($1/s^2$)
- d_h = hydraulic diameter ($s - w$)
- OFA = open frontal area (Nd_h^2)
- GSA = cat. loading area ($4Nd_h$)
- MIF = mechanical integrity factor ($w^2/[(s)(d_h)]$)

Hordozó azonosító:

N/w - cellasűrűség/falvastagság

Cellasűrűség mérőszámok:

cellaszám/coll²

cellaszám/cm²

Characteristics of three commercialized ceramic monoliths

| | | | |
|---|----------------------|----------------------|-----------------------|
| Cell Density (cpsi) / (cpscm) | 100 / 15,5 | 200 / 31,0 | 400 / 62 |
| Wall Thickness (in) / (mm) | 0.017 / 0,432 | 0.012 / 0,302 | 0,0045 / 0,102 |
| Open Frontal Area (OFA) (%) | 34,5 | 34,5 | 84 |
| Geometric Surface Area (GSA) (in ² /in ³) / (m ² /dm ³) | 33.3 / 1,31 | 47.0 / 1,85 | 69 / 2,72 |
| Hydraulic Diameter (in) / (mm) | 0.0813 / 2,11 | 0.059 / 1,49 | 0.0455 / 1,09 |
| Modulus of Rupture (psi/cpscm) | 350 | 300 | |
| Porosity (%) | 48 | 48 | 48 |
| Coefficient of Thermal Expansion (x10 ⁻⁷ cm/cm/°C (25-800°C)) Max average | 5 | 5 | 5 |
| Mean Pore Size (μm) | 13 | 13 | 13 |

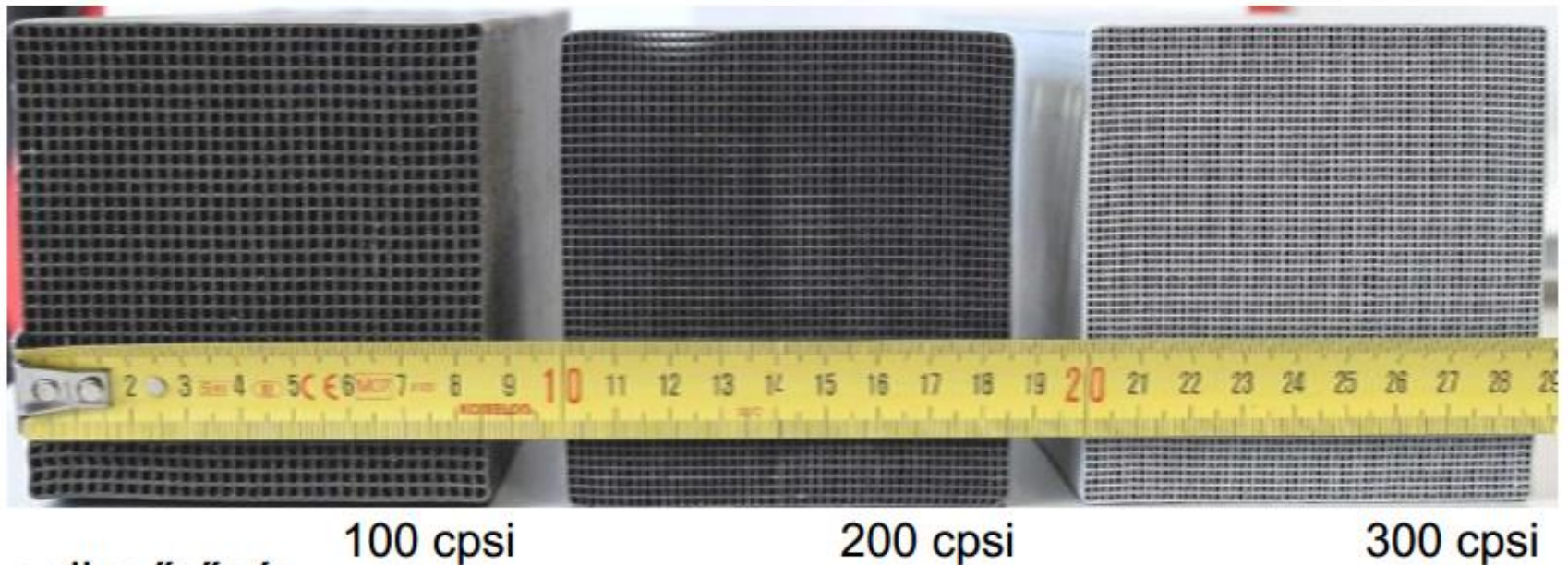
Product Attributes

| Product cpsi/web | Bulk Density [g/L] | Open Frontal Area | Geometric Surface Area [cm ² /cm ³] | Heat Capacity 200° C [J K ⁻¹ L ⁻¹] | Hydraulic Diameter [mm] |
|---------------------|--------------------------|----------------------|--|---|-------------------------------|
| 400/6 | 395 | 0.757 | 27.4 | 352 | 1.11 |
| 350/5.5 | 317 | 0.805 | 26.4 | 283 | 1.22 |
| 400/4 | 279 | 0.828 | 28.7 | 166 | 1.16 |
| 400/3 | 220 | 0.865 | 29.3 | 131 | 1.18 |
| 600/4 | 324 | 0.800 | 34.5 | 193 | 0.93 |
| 600/3 | 267 | 0.836 | 35.3 | 159 | 0.95 |
| 600/2 | 223 | 0.881 | 36.2 | 132 | 0.97 |
| 750/2 | 248 | 0.868 | 40.2 | 148 | 0.86 |
| 900/2 | 271 | 0.856 | 43.7 | 161 | 0.78 |



CORNING

Cellasűrűség (cpsí = cells per square inch)



100 cpsí

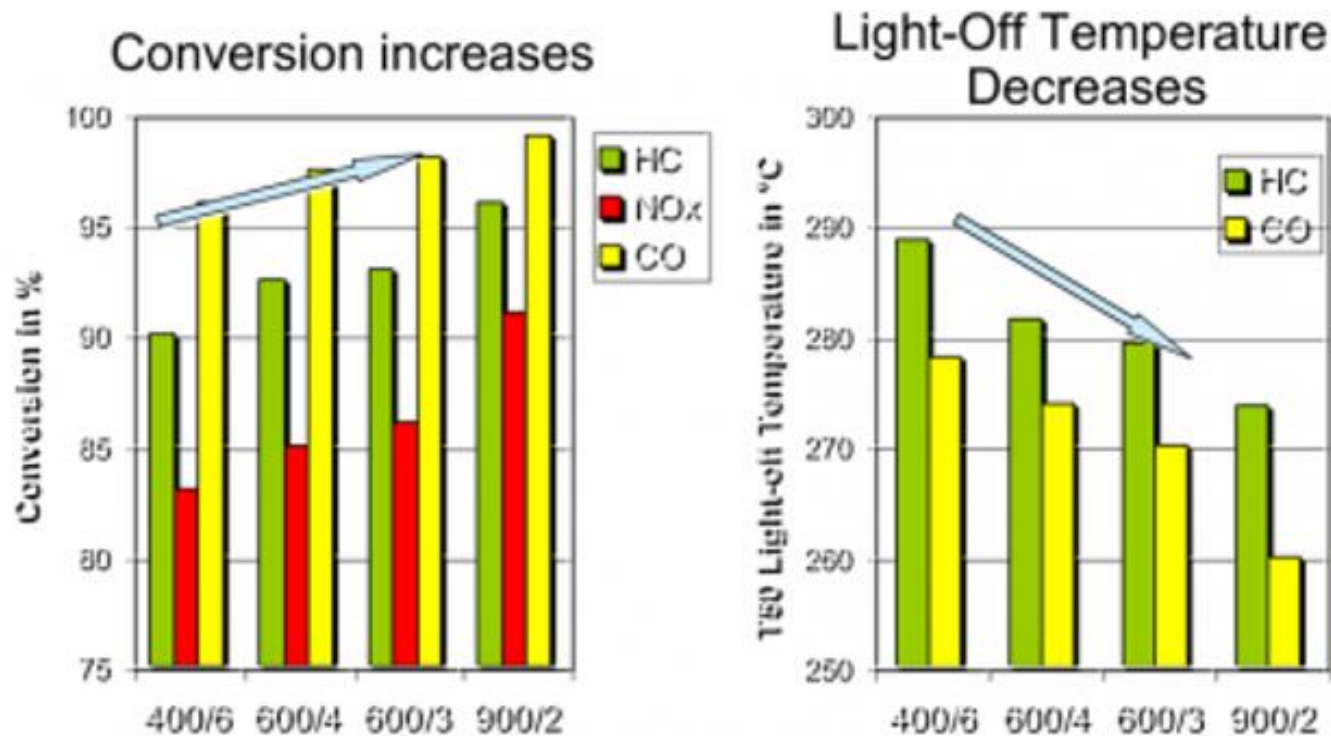
200 cpsí

300 cpsí

Nagy cellasűrűség:

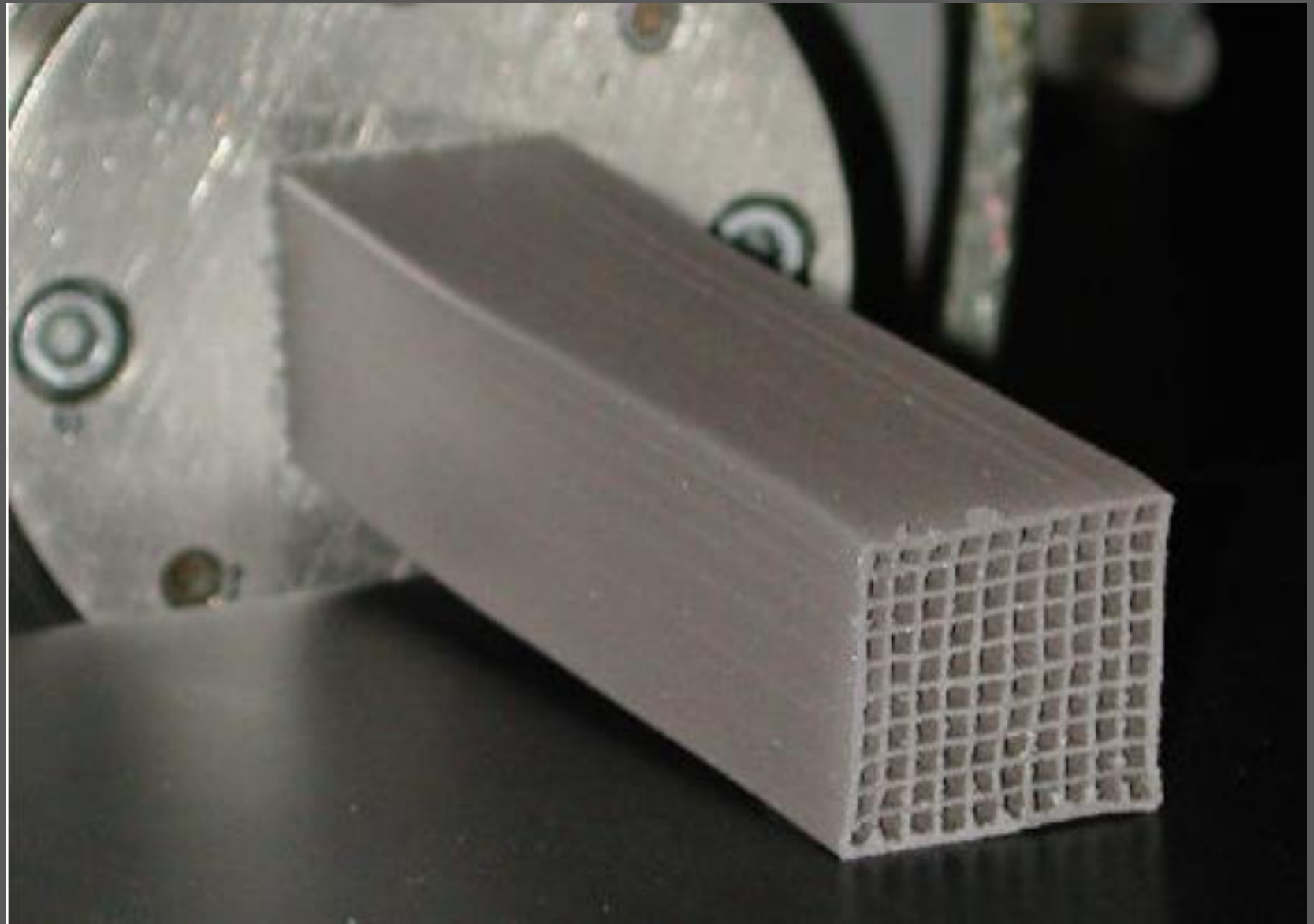
- Ellennyomás megnő
- Felület megnő

- Katalizátor aktivitása megnő
- Koromtároló képesség megnő



A cellasűrűség növelésével és a falvastagság csökkenésével

- nő az átalakítási fok,
- csökken a beindulási hőmérséklet (Light-Off).



A washcoat réteg

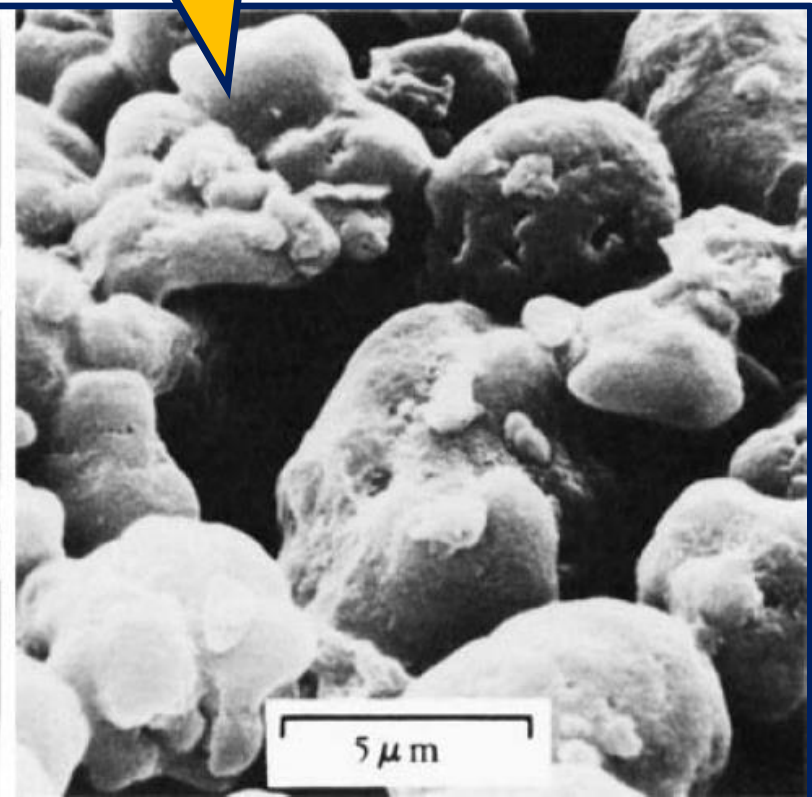
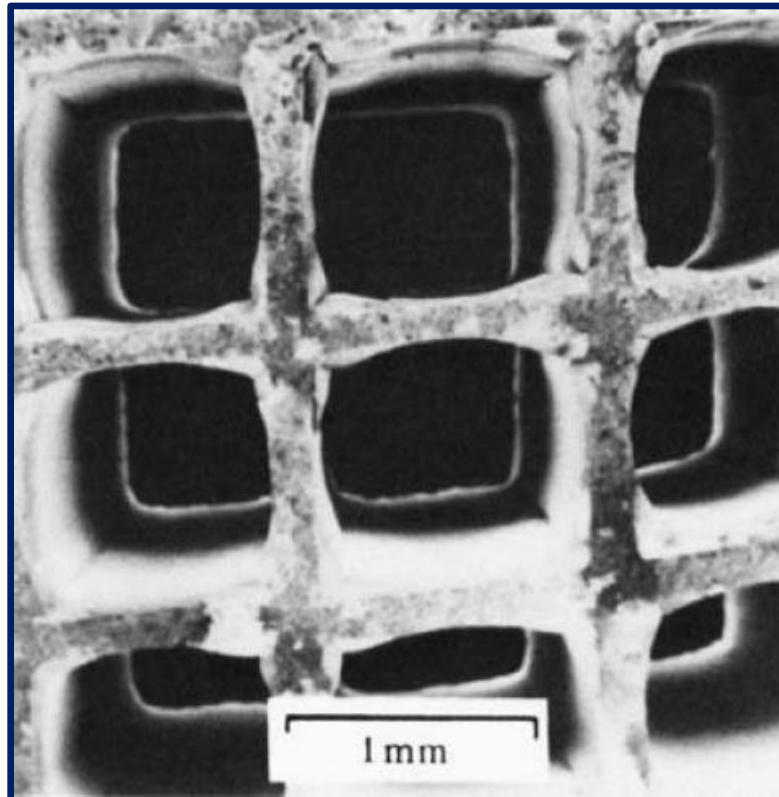
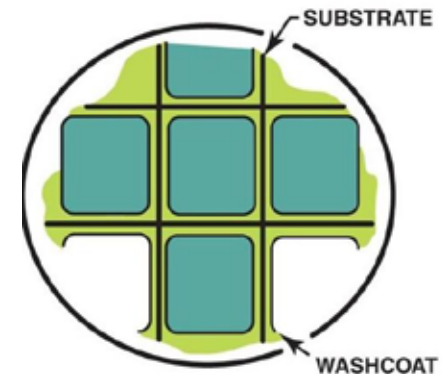
Közbenső réteg/bevonat

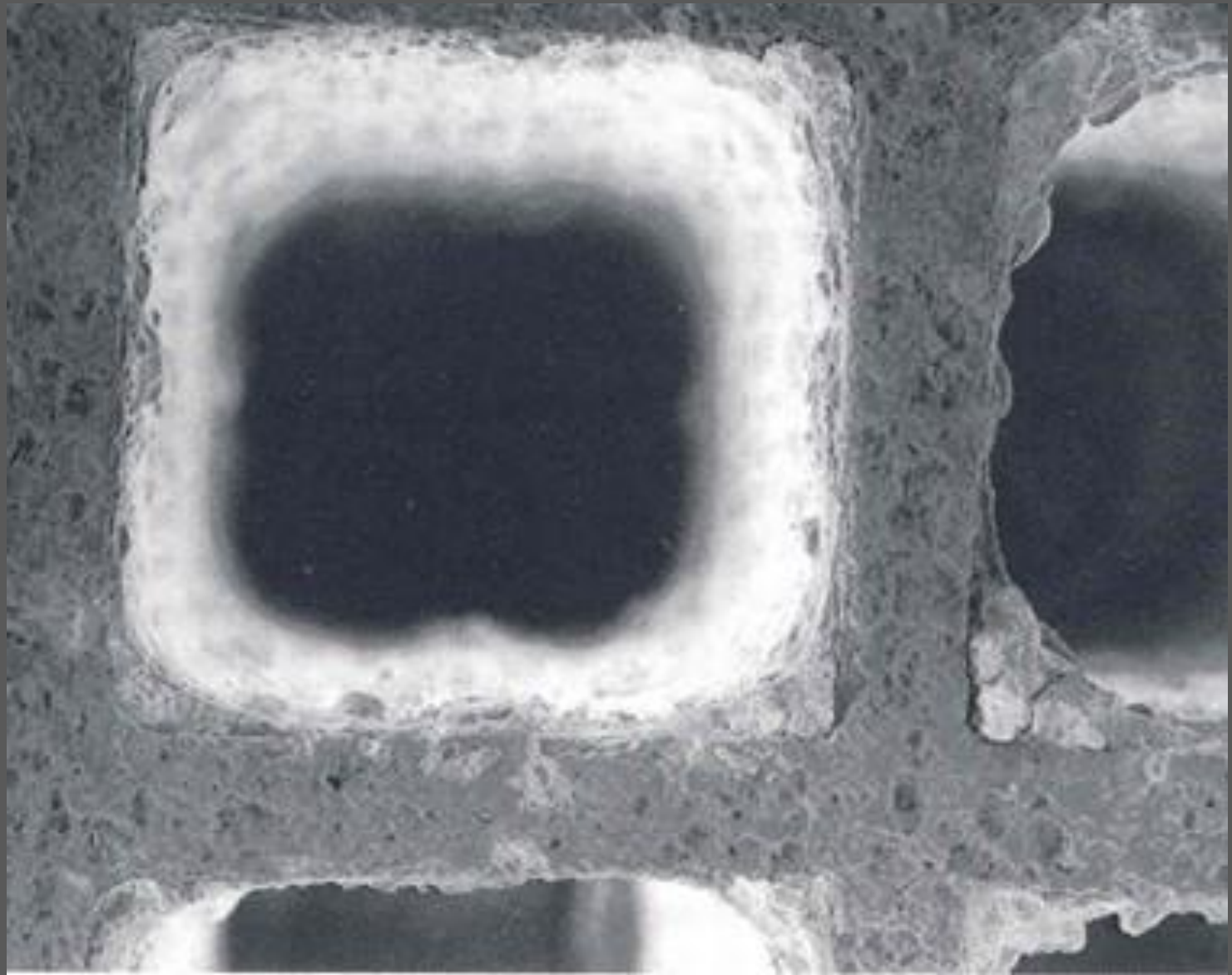
Köztes réteg

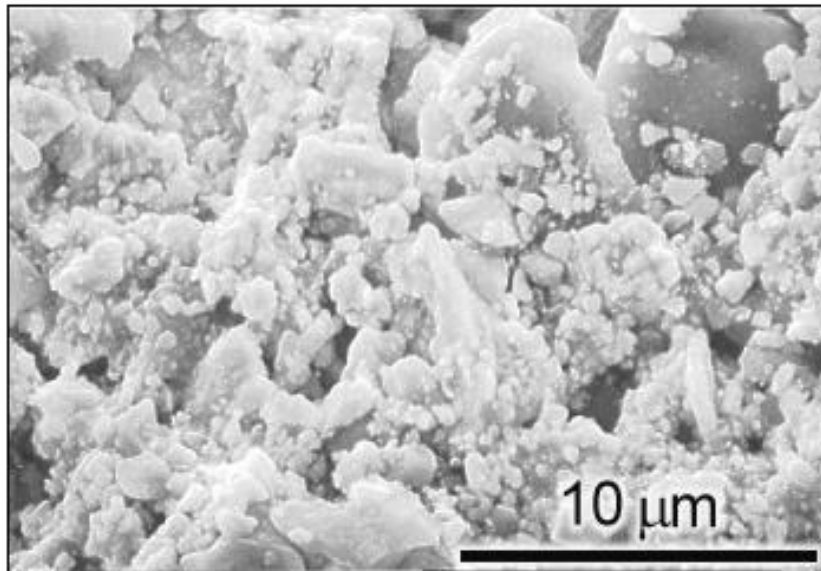
Felületnövelő réteg

Alumina film

Al_2O_3 , SiO_2 , TiO_2 ,
 CeO_2 , ZrO_2 , V_2O_5 ,
 La_2O_3 és zeolitok







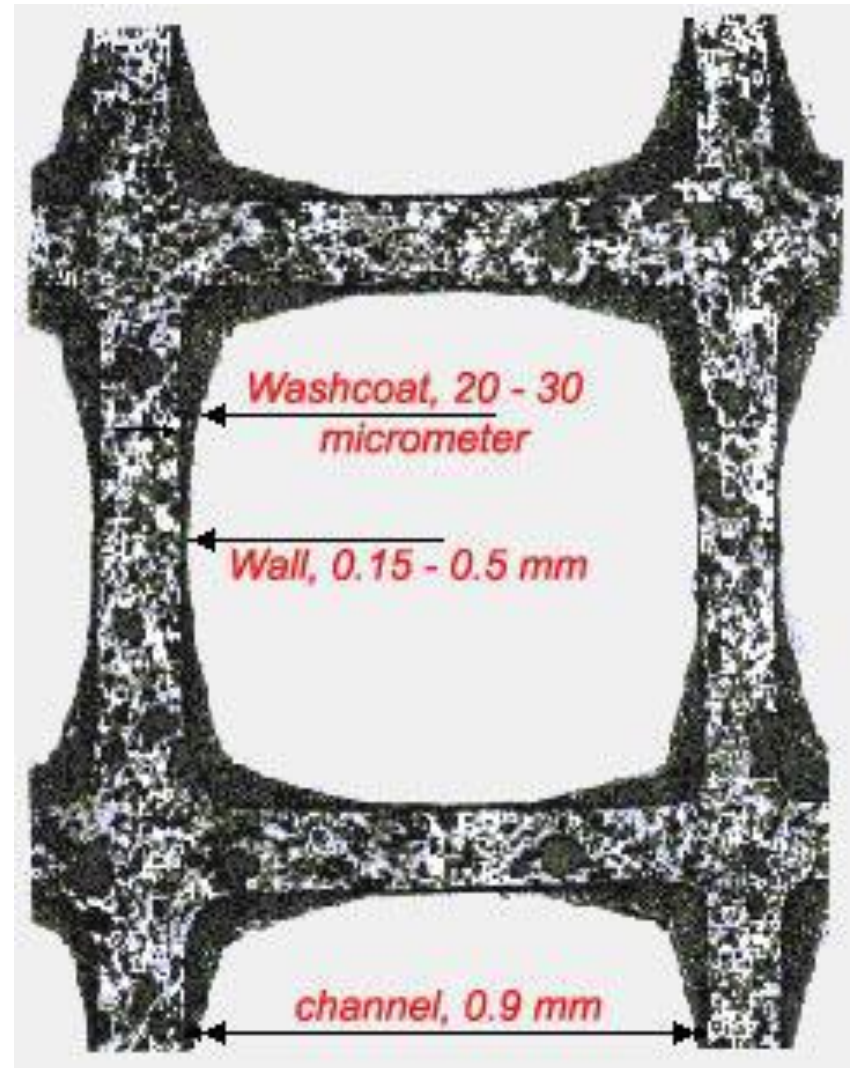
SEM Photograph of Catalyst Washcoat

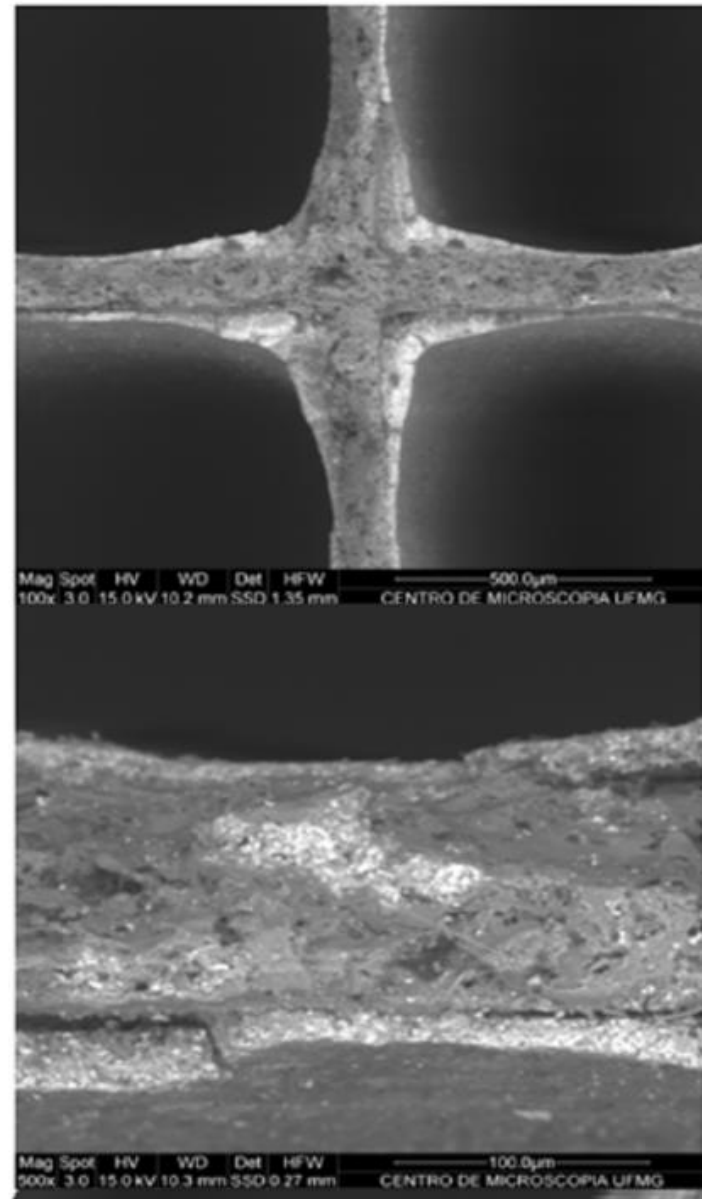
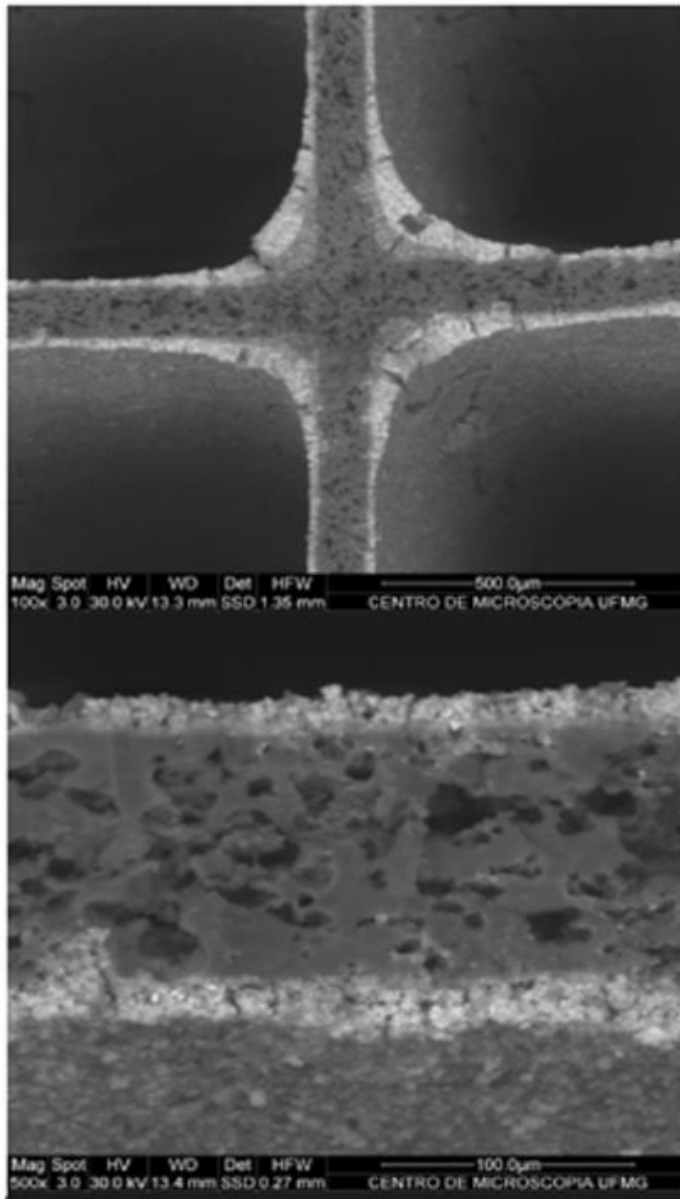
A washcoat réteg vastagsága:

20-40 μm

Fajlagos felülete:

>100 m^2/g



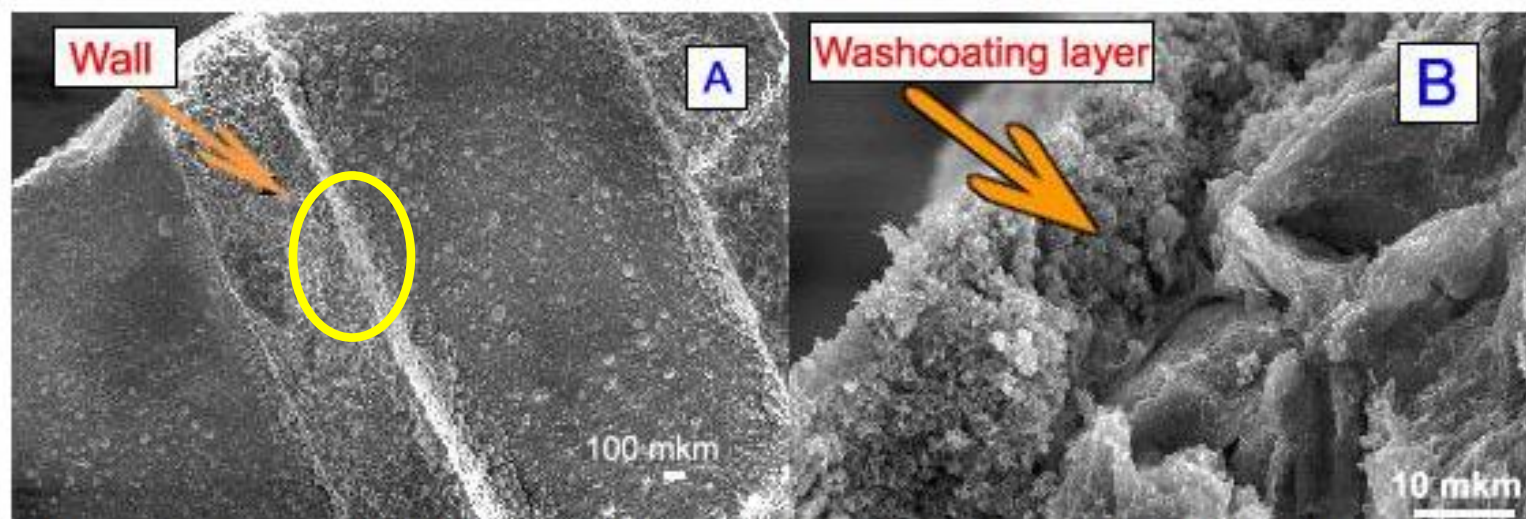


Backscattering SEM micrograph of the alumina film of the (a) new and (b) used automotive catalyst.

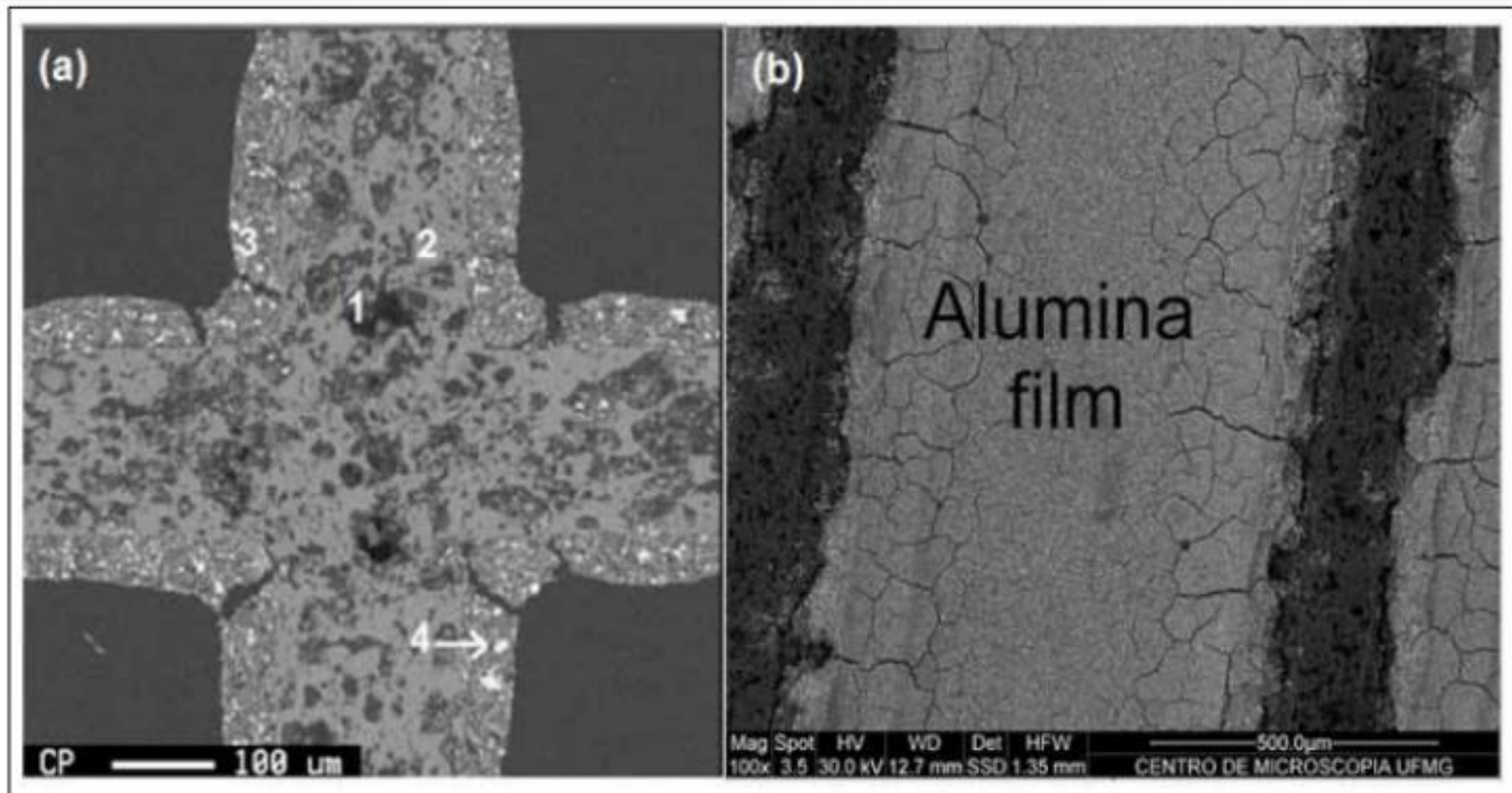
Properties of the monoliths

| Main components /T°C | S _{BET} m ² /g | Phase composition at T°C | Mech. Strength, kg/cm ² | Pore volume (water), cm ³ /g |
|---|------------------------------------|---|------------------------------------|---|
| TiO ₂ / 700°C | 86 | TiO ₂ (anatase) + Al ₂ O ₃ *SiO ₂ | 8 | 0.36 |
| TiO ₂ + ZrO ₂ / 700°C | 69 | TiO ₂ (anatase) + ZrO ₂ (cub.) + Al ₂ O ₃ *SiO ₂ | 13 | 0.36 |
| Alumosilicate / 700°C | 33 | Al ₂ O ₃ *SiO ₂ + α-SiO ₂ | 19.5 | 0.12 |
| Al ₂ O ₃ / 600°C | 190 | γ-Al ₂ O ₃ | 28 | 0.34 |
| H-ZSM-5 / 600°C | 350 | H-ZSM-5 + Al ₂ O ₃ *SiO ₂ | 20 | 0.4 |

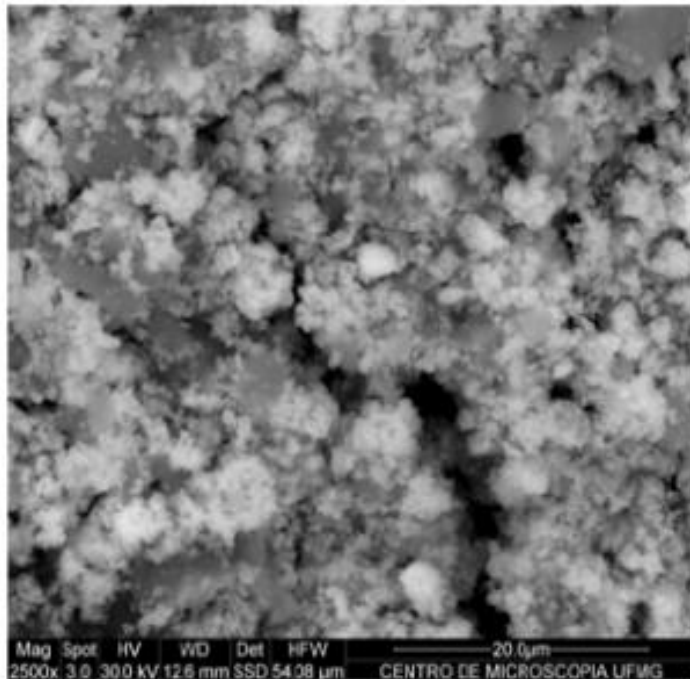
The monoliths based on TiO₂, ZrO₂, and Al₂O₃ still possess relatively high surface area and acceptable mechanical strength that allows their application as supports for monolith catalysts.



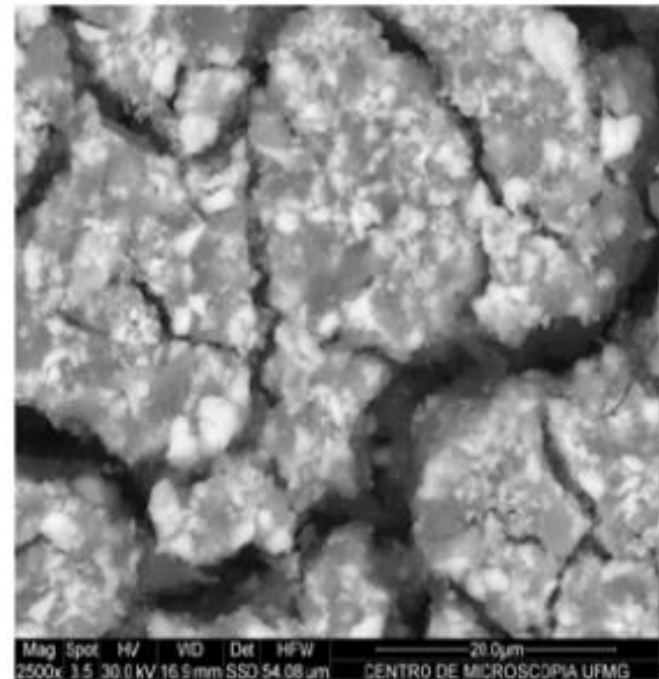
Micrograph of cross-section view of washcoating layer on monolith surface with different enlargement.



(a) Backscattering SEM micrograph of a piece of a new automotive catalyst, and (b) detail of the alumina thin film on the cordierite.

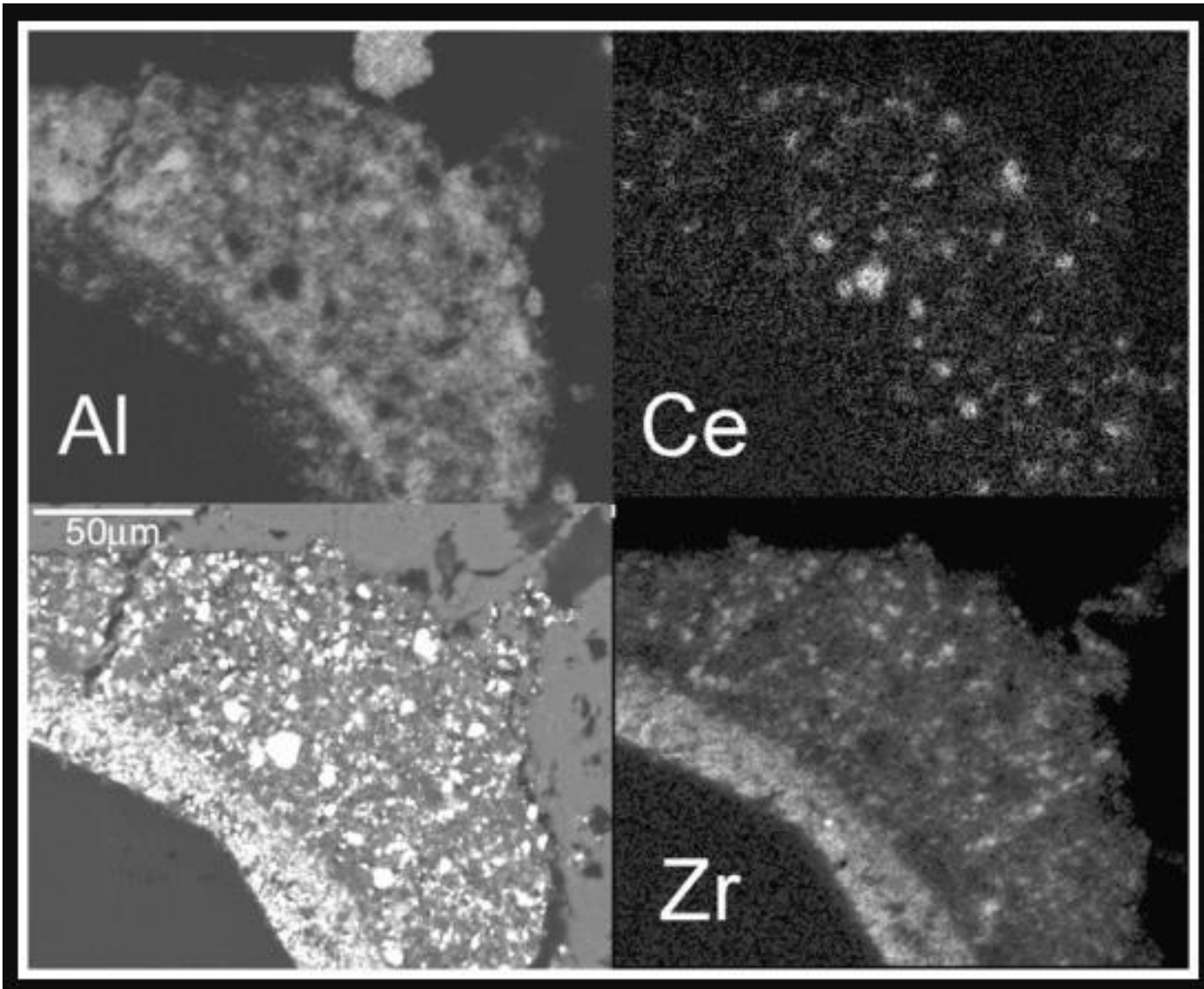


a



b

Backscattering SEM micrograph of the alumina film of the (a) new and (b) used automotive catalyst.

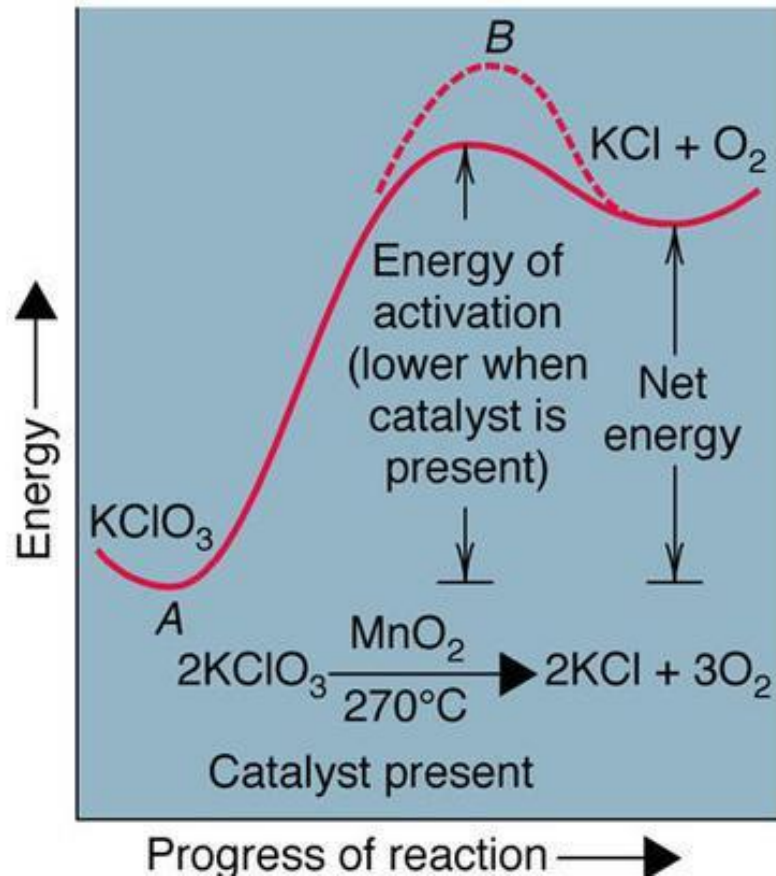


Katalízis



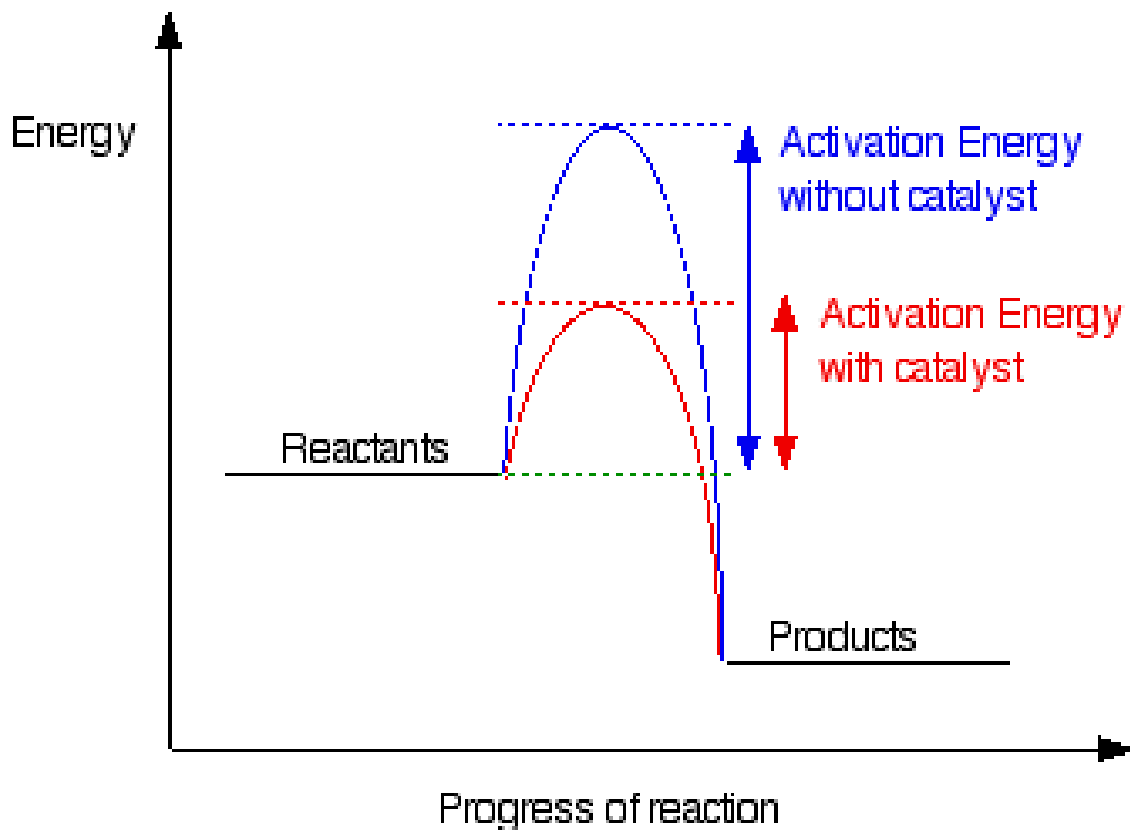
- **Katalizátor**: olyan anyag, amely anélkül változtatja meg a reakció sebességét, hogy ő maga elfogyna a reakcióban.
 - Új reakcióutakat nyit meg.
 - Csökkenti az aktiválási energiát
 - Ugyanazon reaktánsokhoz vezet.
 - Az **enzimek** biológiai katalizátorok.
- **Inhibítor**: Olyan anyag, amely csökkenti a reakció sebességét („negatív” katalizátor)

Katalizátor és a reakció sebessége



- A katalizátor egy adott reakció aktiválási energiáját csökkenti.
- A katalizátor új reakciócsatornát nyit meg.
- A kisebb aktiválási energia miatt a reakció gyorsabban játszódik le.
- Az egyensúlyt nem befolyásolja, **az oda- és vissza reakciót egyformán gyorsítja!**

A katalizátorok a kémiai átalakulás számára új, **kisebb aktiválási energiájú** reakcióutat biztosíthatnak.



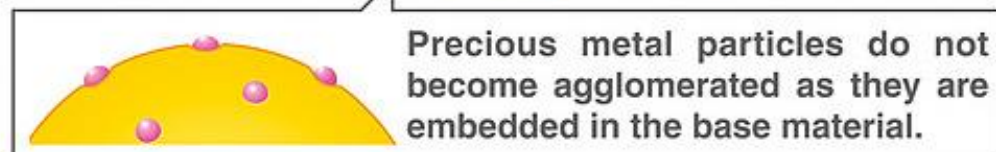
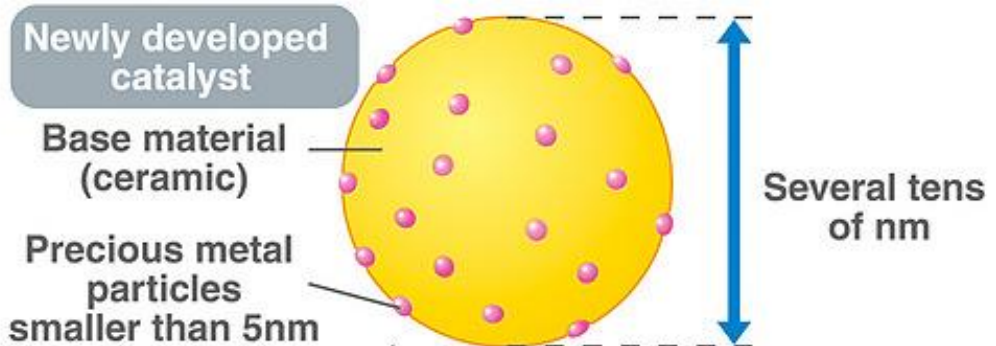
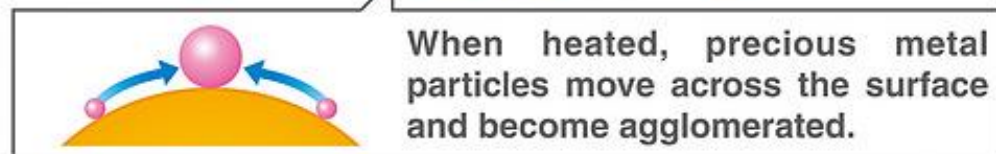
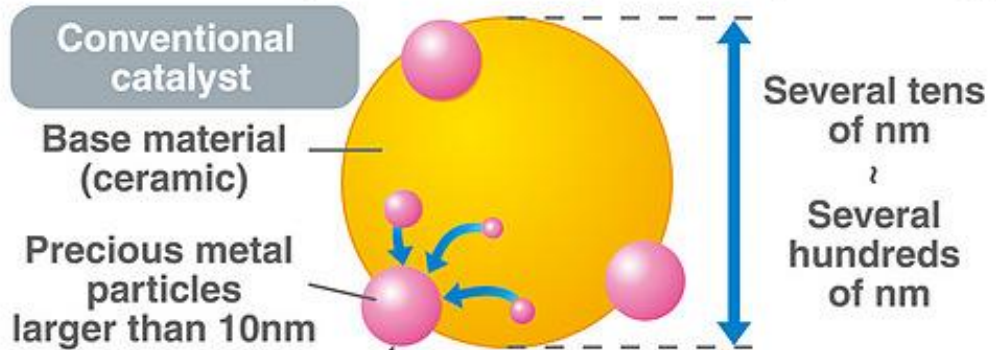
A reakciósebesség mértékegysége: $\text{mol/dm}^3 \times \text{s}$

A cél a katalizátor nemesfémek mennyiségének csökkentése az agglomerálódás megakadályozásával.

Hagyományosan 0,55 g/dm³ helyett a finomelosztatással a **MAZDA** 0,15 g/dm³ értéket ért el.

Precious-metal usage cut with Mazda nanocatalyst
10-Jan-2009 07:01 EST

Precious Metal Dispersion Achieved by New Catalyst Technology



The recoverable amounts of Pt, Pd, and Rh in each can range from 1-2 grams for a small car to 12-15 grams for a big truck.

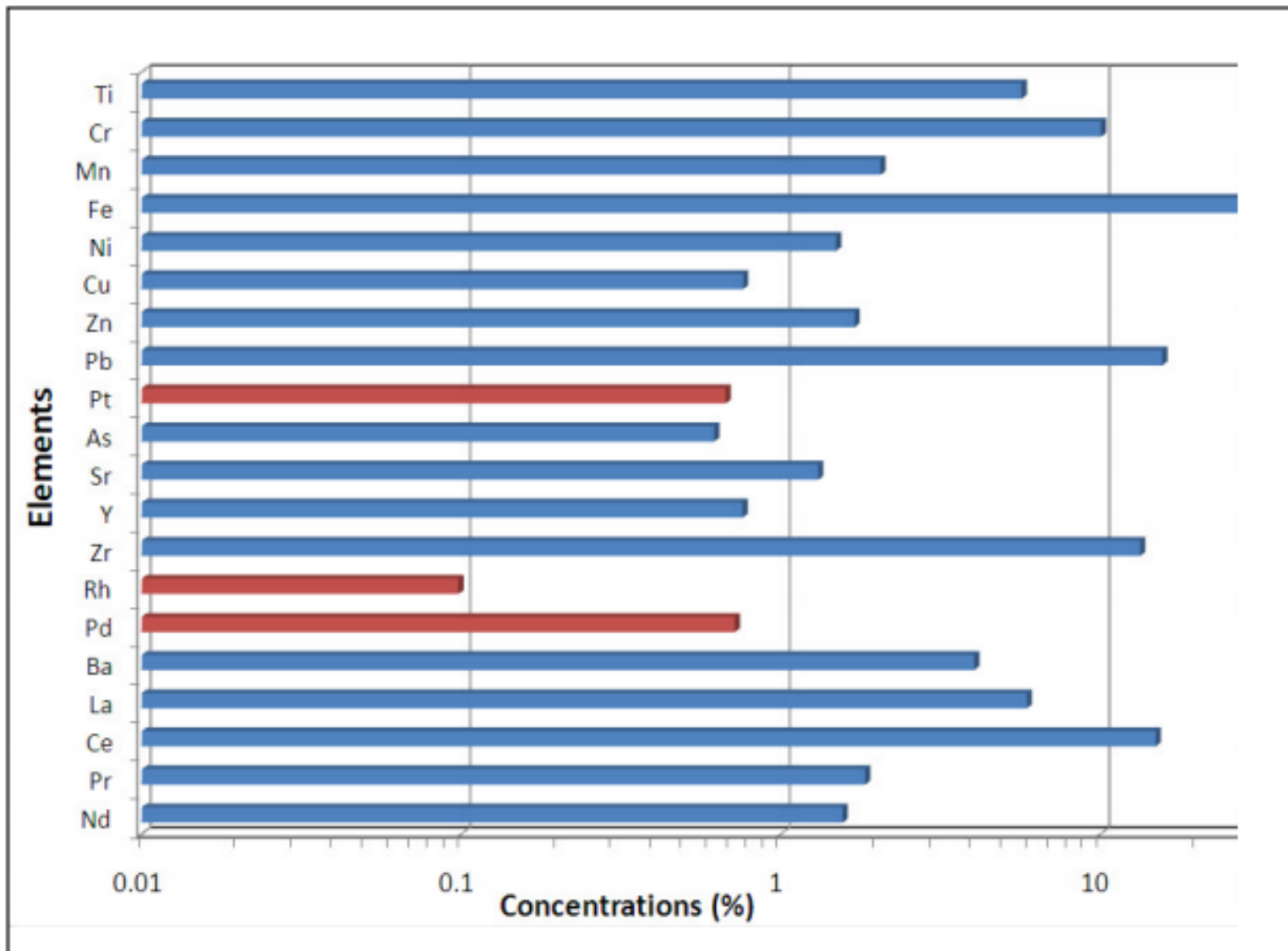
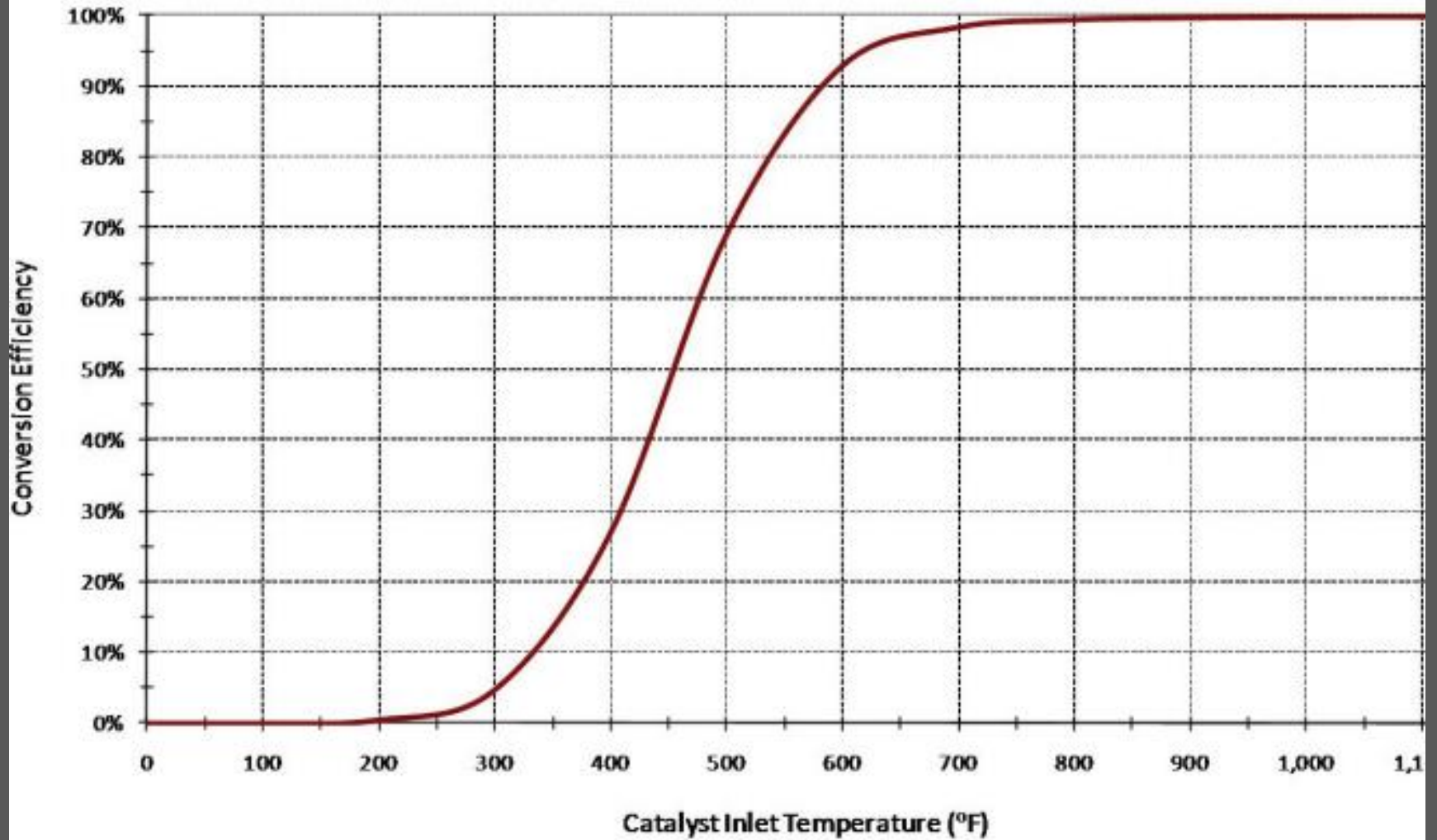
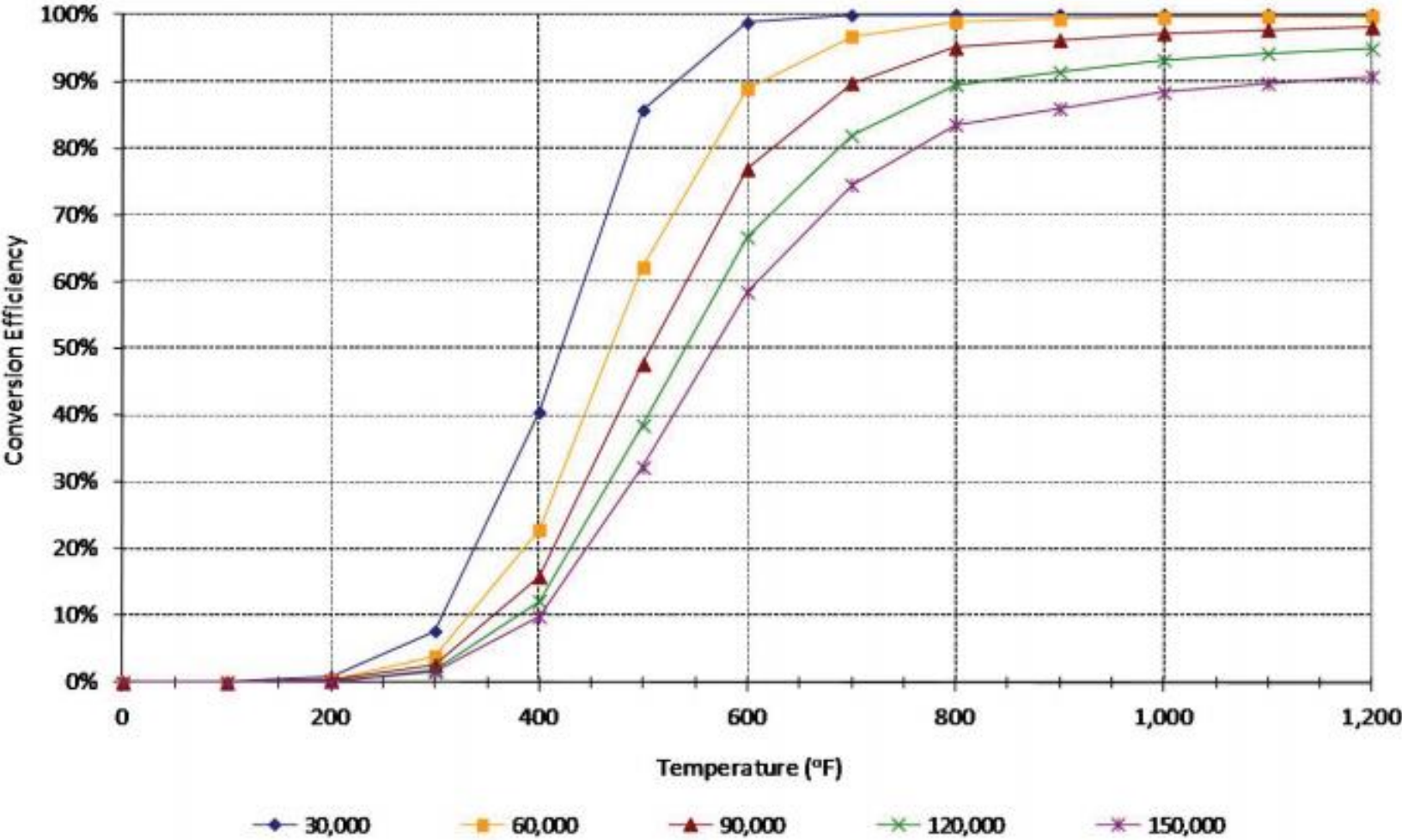


Figure 5. Range of concentration for Pt, Pd, Rh and relevant matrix elements found in the investigated samples

Conversion Efficiency vs. Catalyst Inlet Temperature

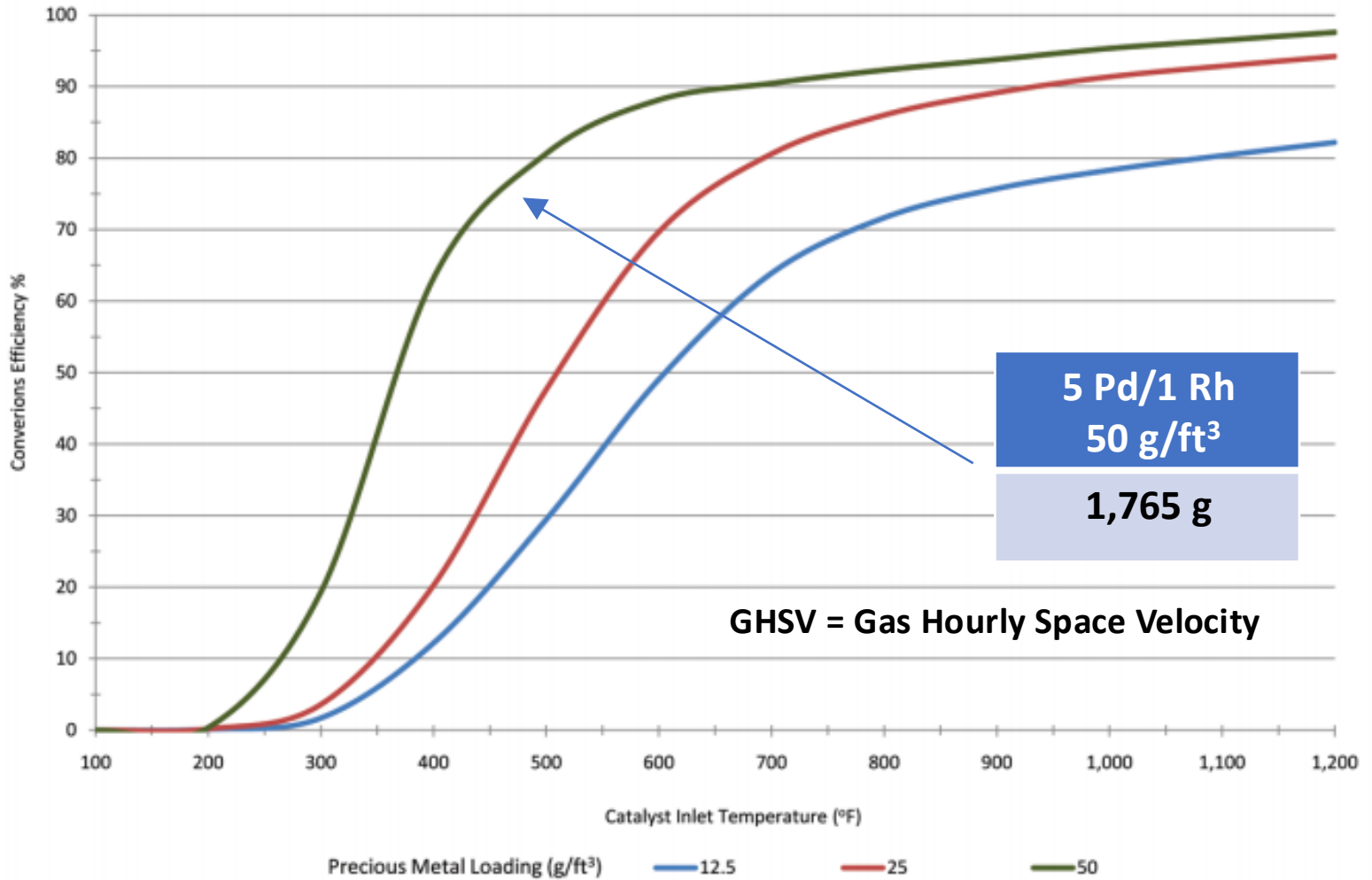


Catalytic Activity as a Function of Space Velocity



Effect of Precious Metal Loading on Catalyst Performance

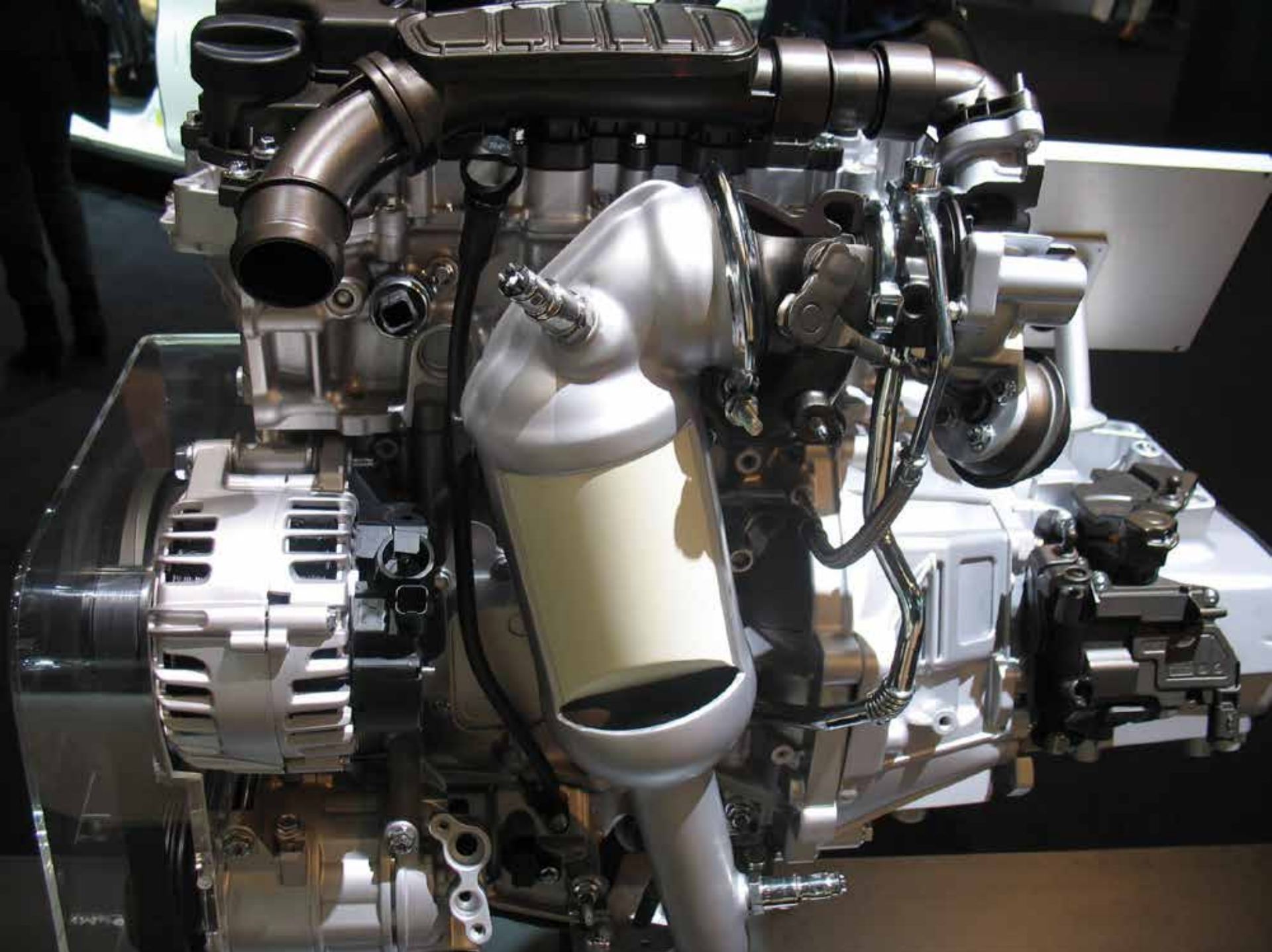
GHSV = 150,000 hr⁻¹







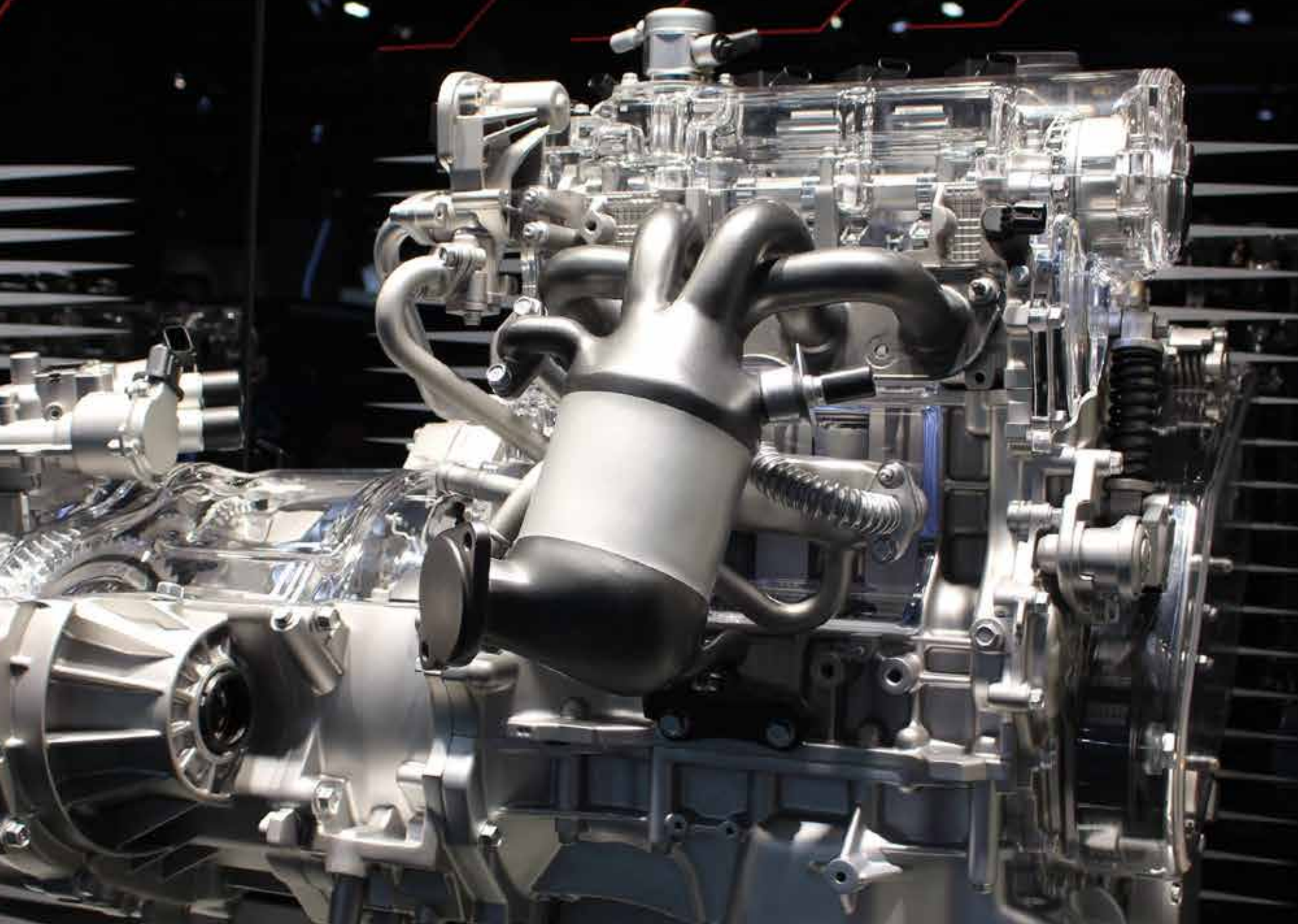




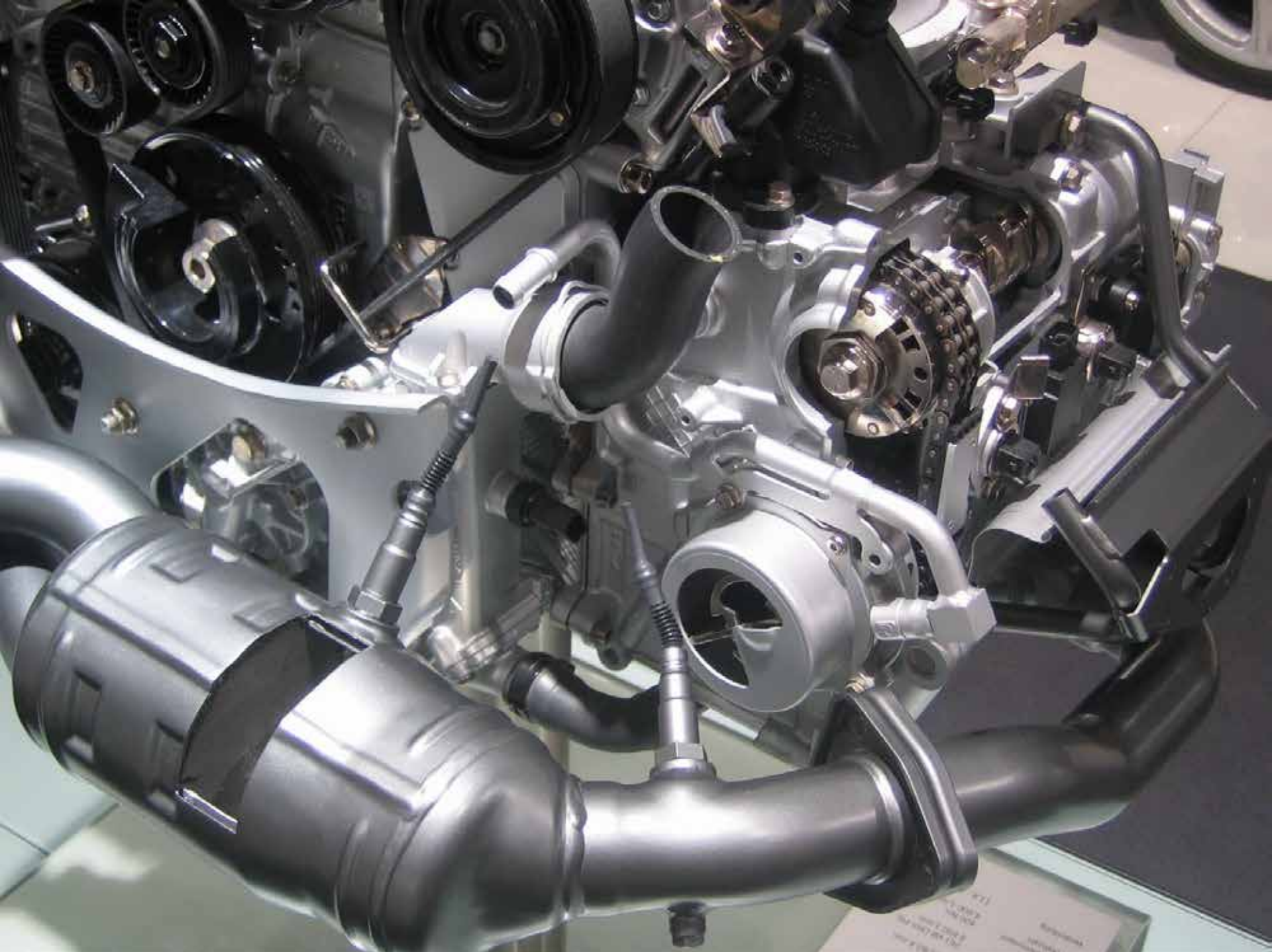


at

1353 ccm







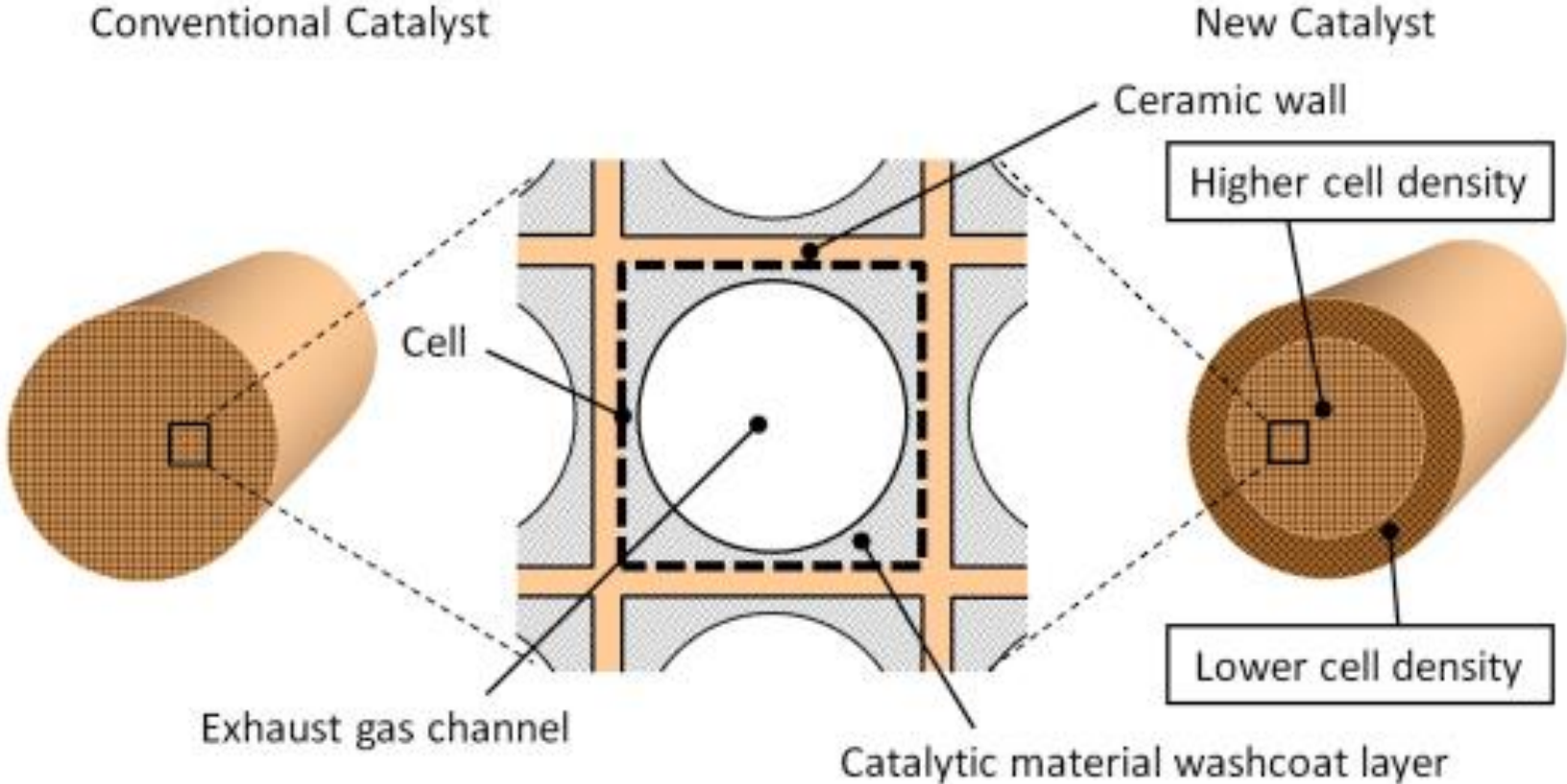
711
PARTS
FOR THE
711

Új TWC katalizátor kialakítások

Flow Adjustable Design Cell (FLAD[®]) substrate

FLAD is a registered trademark of Denso Corporation.

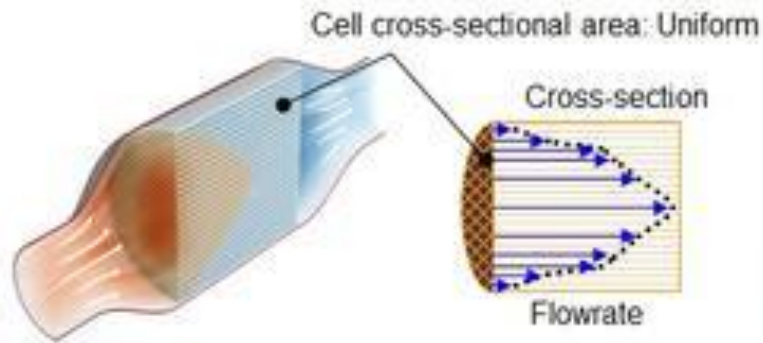
Catalyst Structure



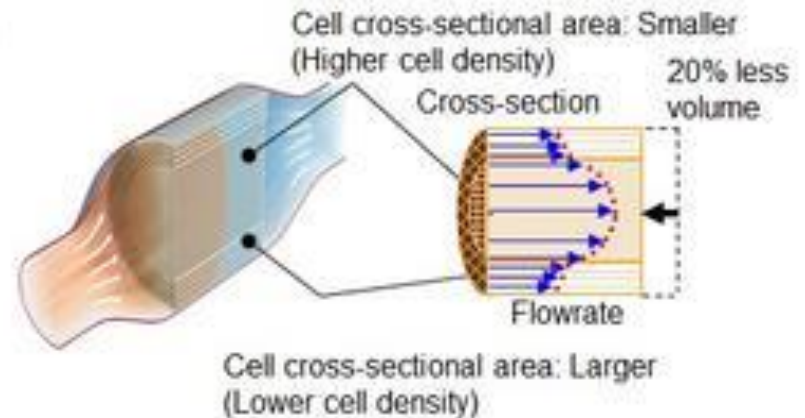
*New catalyst is world's first integrally molded FLAD® substrate
Groundbreaking design reduces catalyst volume by 20 percent*

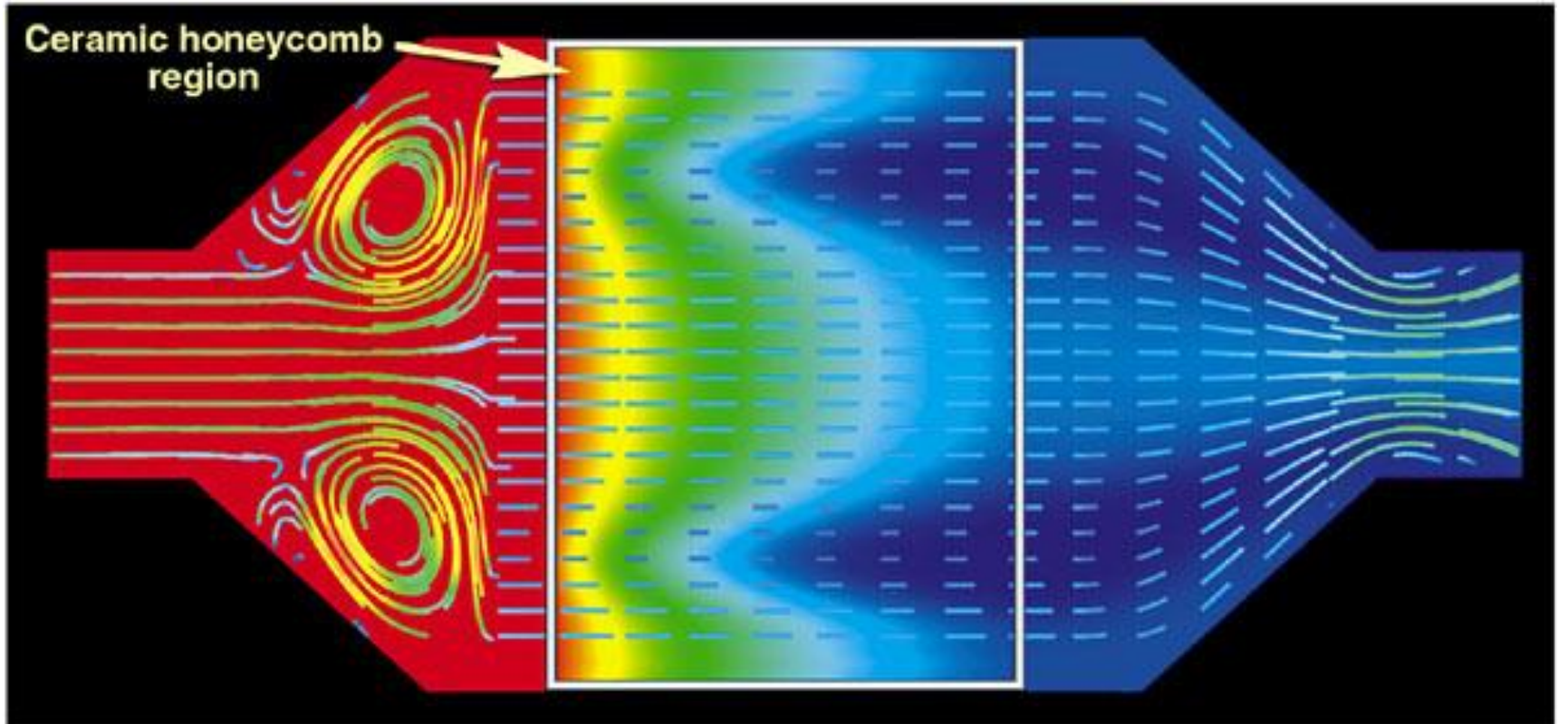
Flow of exhaust gas within the catalyst

Conventional Catalyst



New Catalyst

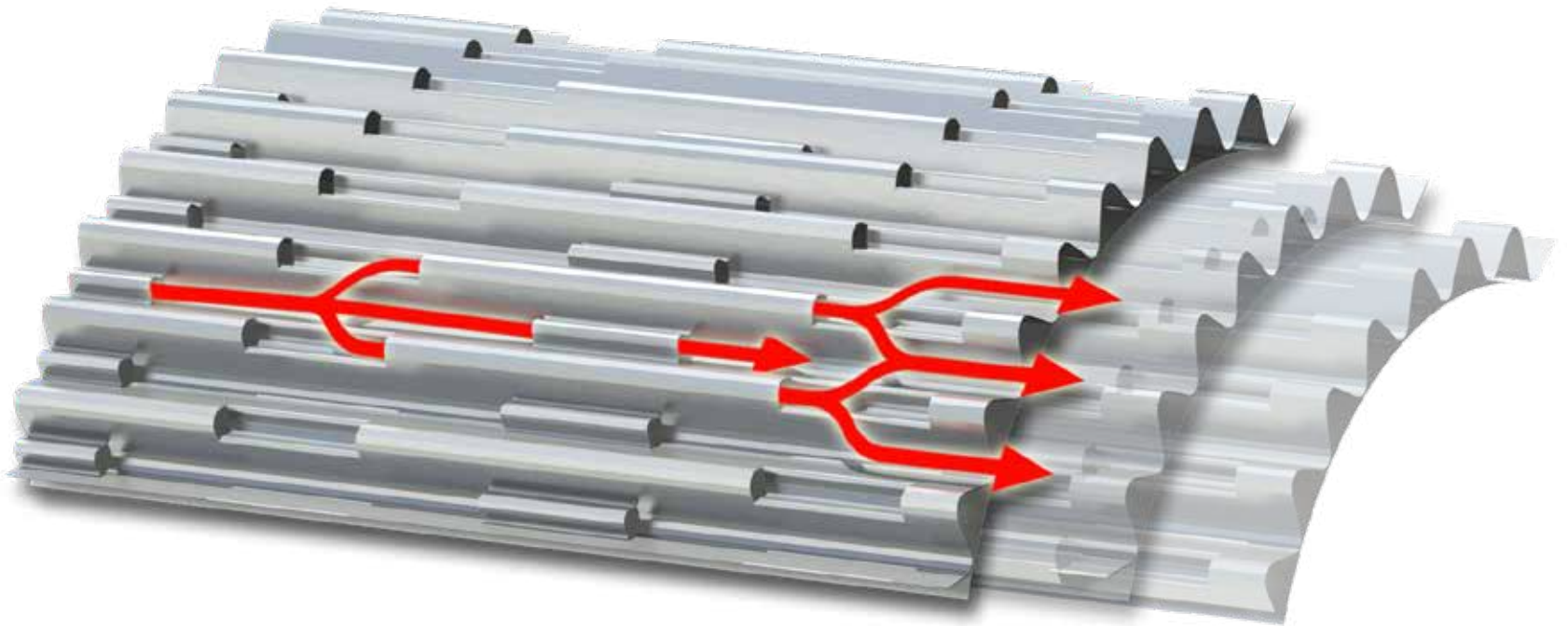




Continental Ring catalyst



The core of the catalytic converter is wound from “LS” metal foil, a material developed by Continental. Longitudinal structures (= LS) in this foil or substrate create more turbulence in the exhaust gas. This ensures better contact between the nitrogen oxides and the catalytically coated substrate, resulting in higher conversion efficiency.





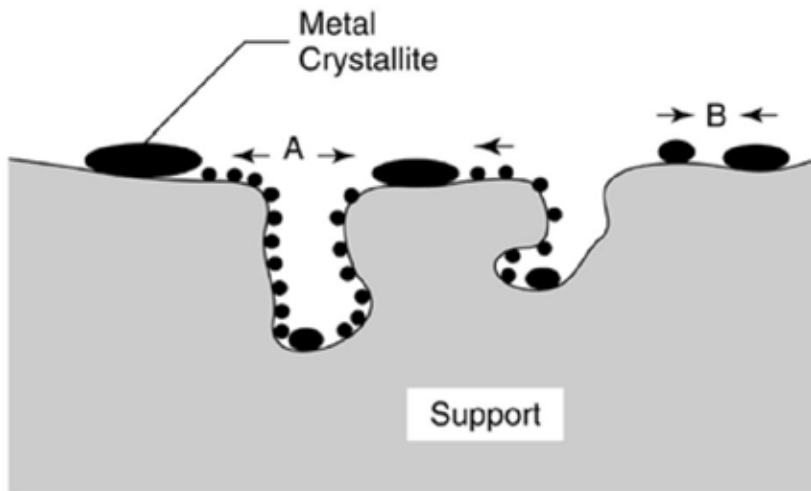


TWC PM szűrővel

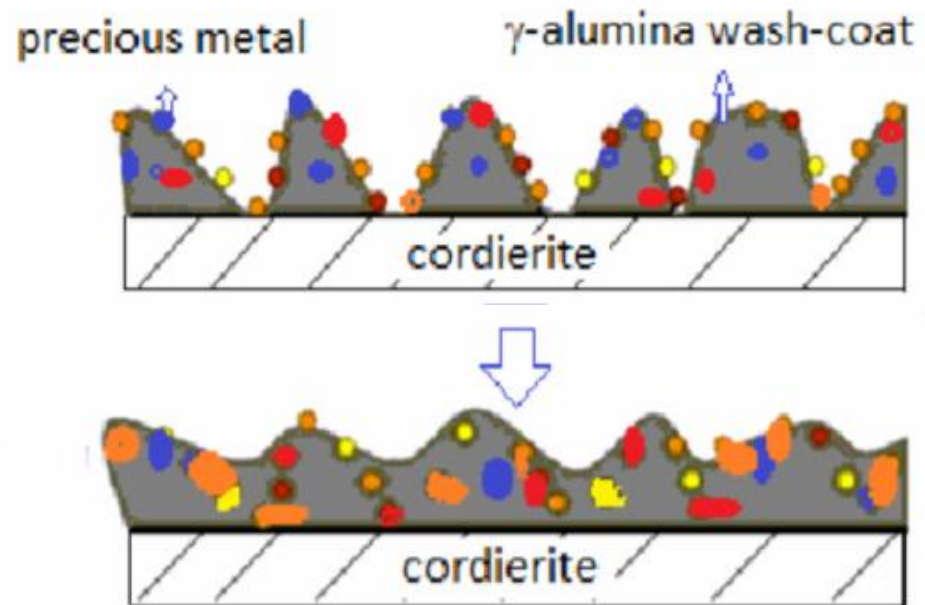
Erről később lesz szó

A katalizátor meghibásodásai

- Mechanikai sérülés
 - kerámiahordozó (monolit) törés
 - fémhordozó (fémmonolit) deformáció
- Katalizátor mérgeződés
 - pl. ólom, kén, foszfor
- Katalizátor hatásfok veszteség
 - nemesfém szintereződés
- Termikus túlterhelés
 - washcoat finomszerkezet
 - wash coat leolvadás
 - hordozóanyag lágyulás, megolvadás



Schematic illustration of the catalyst deactivation due to the thermal effects.

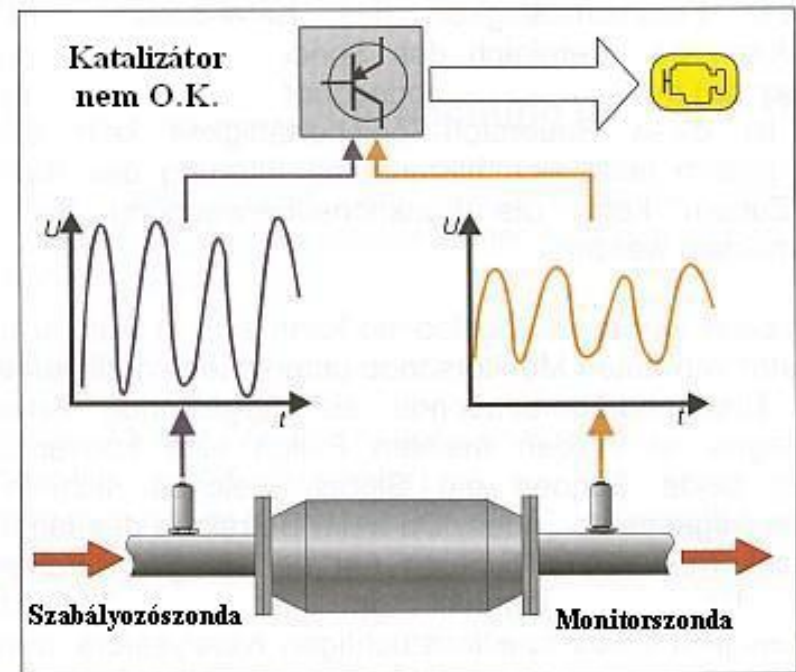
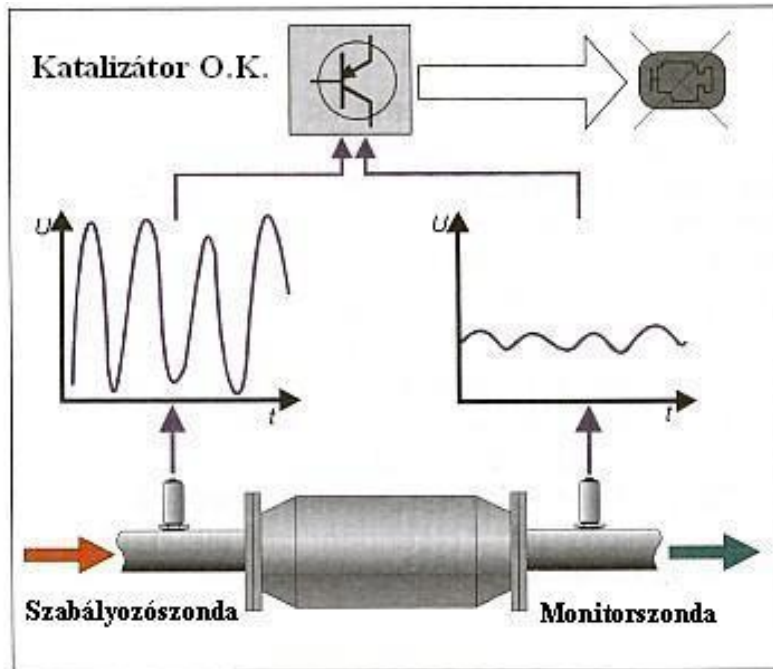


A 3-komponensre ható katalizátor (TWC) fedélzeti diagnosztikája (OBD-felügyelet)

Ha a katalizátor előregedett az oxigéntároló képessége is erőteljesen lecsökken.

Jó állapotban a monitorszonda csekély oxigént, kis amplitúdójú koncentráció hullámzást mutat.

Kis hatékonyságú állapotban leköveti a katalizátor belépési oxigénkoncentrációt!









**A szomorú
vég...**

Katalizátor termikus függése

| | | |
|------|--|--|
| 1400 | Túlmelegedés | A hordozó olvadáspontja : 1380 °C |
| 1200 | Igen erős dezaktiválás | a hordozó részleges károsodása, lágyulása: 1200-1300 a wash-coat leválása 1200 °C -tól kezdődően, a Pt és Rh kristályosodása |
| 1100 | Átmeneti állapot Jelentős termikus dezaktiválás /öregedés/ Gyenge kémiai dezaktiválás /öregedés/ Átlagos termikus tartomány dezaktiválás /öregedés/ | a γ -alumínium zsugorodása |
| 800 | Működési tartomány Átlagos termikus tartomány dezaktiválás /öregedés/ Gyenge kémiai dezaktiválás /öregedés/ | |
| 600 | Gyenge termikus dezaktiválás /öregedés/ Jelentős kémiai dezaktiválás /ólom, cink, foszfor, kalcium, magnézium hatására/ | optimális működési tartomány |
| 400 | | |
| 270 | Előregedett katalizátor indulási hőmérséklete | |
| 230 | Új katalizátor indulási hőmérséklete | |
| 200 | Nem aktív hőmérséklettartomány | 30-90 s a hidegindítás után |

Vége